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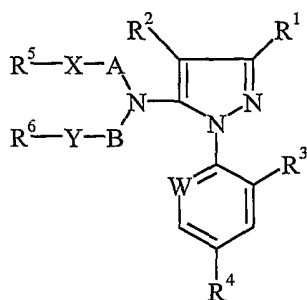
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(54) Title: PESTICIDAL 5-DI-(SUBSTITUTED)AMINOPYRAZOLE DERIVATIVES



(I)

(57) Abstract: Certain novel 5-di-(substituted)aminopyrazole derivatives have unexpected activity in controlling insects, general household pests and animal parasites. These compounds are represented by formula I: where A, B, W, X, Y and R through R6, inclusively, are fully described herein, in addition, compositions comprising a pesticidally effective amount of at least one compound of formula I, and optionally, an effective amount of at least one of an additional compound, with at least one pesticidally compatible carrier are also disclosed; along with methods of controlling pests comprising applying said compositions to a locus where pests are present or are expected to be present.

PESTICIDAL 5-DI-(SUBSTITUTED)AMINOPYRAZOLE DERIVATIVES

This application claims the benefit of U.S. Provisional Application No. 60/690,014 filed June 13, 2005, and U.S. Provisional Application No. 60/763,071, filed January 27, 2006.

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FIELD OF THE INVENTION

The present invention relates to novel compounds and their use in controlling pests such as insects, acarids, general household pests and animal pests. In particular, it pertains to 5-di-(substituted)aminopyrazole derivatives, insecticidally acceptable salts thereof, compositions containing them and methods for their use in controlling agricultural pests. The invention also relates to 5-di-(substituted)aminopyrazole derivatives, pesticidally acceptable salts thereof, compositions containing them and methods for their use in controlling general household pests. The invention also relates to 5-di-(substituted)aminopyrazole derivatives, veterinarily acceptable salts thereof, compositions containing them and methods for their use in controlling parasites in or on domestic and non-domestic animals.

BACKGROUND OF THE INVENTION

It is well known that insects in general can cause significant damage, not only to crops grown in agriculture, but also, for example, to structures and turf where the damage is caused by soil-borne insects, such as termites and white grubs. Such damage may result in the loss of millions of dollars of value associated with a given crop, turf or structures. Insecticides and acaricides are useful for controlling insects and acarids which may otherwise cause significant damage to crops such as wheat, corn, soybeans, potatoes, and cotton to name a few. For crop protection, insecticides and acaricides are desired which can control the insects and acarids without damaging the crops, and which have no deleterious effects to mammals and other living organisms.

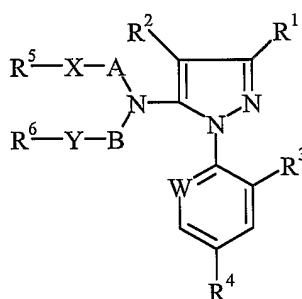
It is generally a goal of veterinarians to possess sufficient means to control parasites, particularly arthropods or helminths, when they attempt to invade or attack animals, particularly domestic animals and/or livestock. A classical method of controlling such parasites has been the use of topical and/or systemic pesticides on

or in the animal which is being attacked. Generally effective treatments include the oral administration of insect growth regulators, such as lufenuron, antihelminth compounds such as an ivermectin or avermectin or the topical application of the insecticide fipronil.

5 The control of insects, arachnids and helminths with 1-arylpyrazole compounds has been described in, for example, patent publication numbers WO 98/28277, WO 98/282278, EP 500209, EP 295117, U.S. 5,814,652 and U.S. 5,232,940. The control of parasites in animals with 1-arylpyrazole compounds has been described in, for example, patent publication numbers WO 03/074492, WO
10 03/074493, WO 00/35884, WO 97/28126, U.S. 6,069,157, and U.S. 6,531,501.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been found that certain novel 5-di-(substituted)aminopyrazole derivatives are surprisingly active in the control of
15 insects, acarids, general household pests and domestic and non-domestic animal parasites when used in the pesticidal compositions and methods of this invention. The novel derivatives are represented by the following general formula I:



I

20

wherein

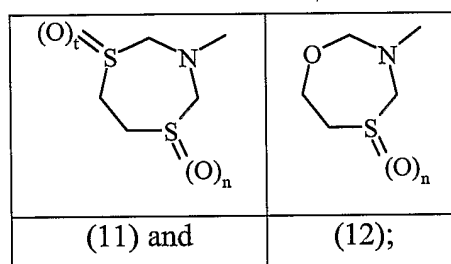
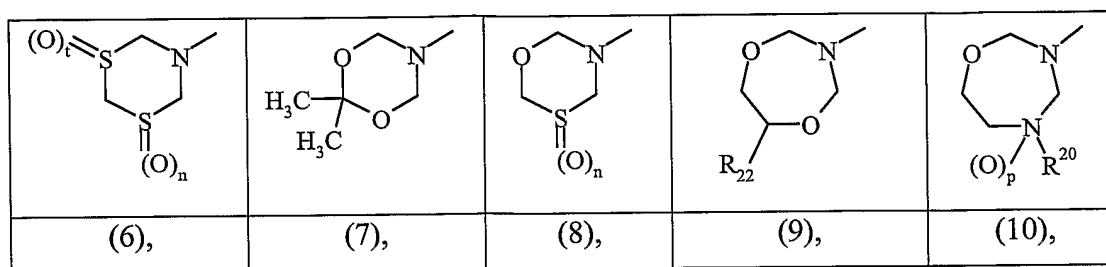
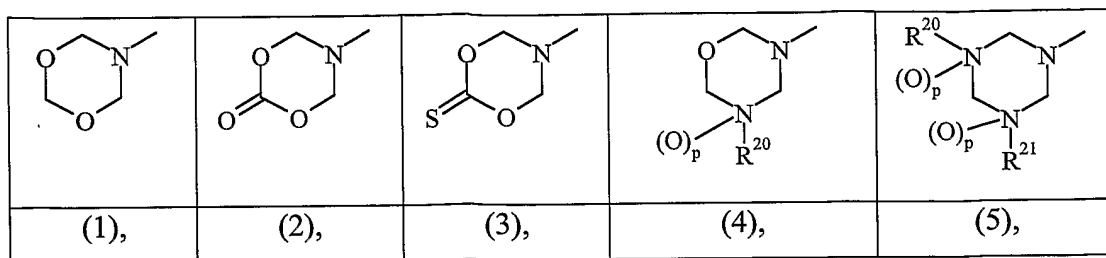
W is C-halogen, C-CH₃, C-CH₂F, C-CHF₂, C-CF₃, C-NO₂ or N;

R¹ is selected from halogen, cyano, (C₁-C₄)alkyl, (C₁-C₄)haloalkyl, (C₃-

25 C₆)cycloalkyl, -S(O)_nR¹⁰, formyl, acetyl, nitro, -C(S)NH₂, -C(=NNH₂)NH₂; or
R¹ is -CR⁷=N-O-Y¹, wherein R⁷ is hydrogen, alkyl or R⁷ and Y¹ are taken together to form a 5 or 6 member ring or R⁷ is -NR⁸R⁹, wherein R⁸ and R⁹ are independently hydrogen or alkyl and Y¹ is hydrogen, alkenyl, alkynyl, formyl, alkylcarbonyl, cycloalkylcarbonyl, haloalkylcarbonyl, aroyl, arylalkylcarbonyl, alkylsulfonyl, arylsulfonyl, haloalkylcarbonyl, aminoalkylcarbonyl,

- alkylaminoalkylcarbonyl, dialkylaminocarbonyl, alkoxyalkylcarbonyl, arylalkoxycarbonyl, alkylthioalkylcarbonyl, alkylsulfonylalkylcarbonyl, arylthioalkoxycarbonyl, N-alkylcarbamoyl, N-arylcarbamoyl, N-alkylthiocarbamoyl, N-arylthiocarbamoyl, alpha-hydroxyarylalkylcarbonyl, hydroxyalkylcarbonyl, carboxyalkylcarbonyl, alkoxycarbonylalkylcarbonyl, -P(=O)(O-alkyl)₂, -P(=S)(O-alkyl)₂, -P(=O)(S-alkyl)₂, trialkylsilyl, alkylcarbonylaminoalkylcarbonyl, alkylcarbonyloxyalkylcarbonyl, aryl, pyridinyl, pyrimidinyl, -C(=O)S-alkyl, -C(=O)S-aryl, -C(=O)S-alkylaryl, alkoxyalkoxycarbonyl, alkylthioalkoxycarbonyl, alkylsulfonylalkoxyoxycarbonyl, arylthioalkoxycarbonyl, alkoxycarbonyl, aryloxy carbonyl and aryloxy carbonylalkylcarbonyl; or alkyl or haloalkyl, optionally substituted by alkoxy, alkoxycarbonyl, carboxy, cyano, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylthio, nitro, alkylsulfinyl, alkylsulfonyl, alkylcarbonyl, amino, alkylamino, dialkylamino, hydroxy, alkylcarbonylamino or alkylcarbonyloxy;
- R² is selected from hydrogen, halogen, -S(O)_nR¹⁰, (C₁-C₄)alkyl, (C₁-C₄)haloalkyl, (C₃-C₅)alkenyl, (C₃-C₅)haloalkenyl, (C₃-C₆)cycloalkyl, (C₃-C₆)halocycloalkyl, (C₃-C₅)alkynyl, aryl, heteroaryl, -NR⁸R⁹, -CO₂R¹⁵, -CR⁷=N-O-Y¹, nitro or cyano;
- n is an integer selected from 0, 1 and 2;
- R³ is hydrogen, halogen, cyano, formyl, acetyl, alkyl, haloalkyl or nitro;
- R⁴ is halogen, (C₁-C₄)alkyl, (C₁-C₄)haloalkyl, (C₃-C₅)alkenyl, (C₃-C₅)alkynyl, (C₁-C₄)alkoxy, (C₁-C₄)haloalkoxy, -S(O)_nhaloalkyl or -SF₅;
- A and B are independently selected from alkylene and haloalkylene;
- X and Y are independently selected from O, N-R¹¹, N(O)-R¹³, SiR¹⁰R¹⁰, and S(O)_n;
- R⁵ and R⁶ are independently selected from hydrogen, (C₃-C₅)alkenyl, (C₃-C₅)haloalkenyl, (C₃-C₅)alkynyl, (C₃-C₅)haloalkynyl, (C₃-C₆)cycloalkyl, -(CH₂)_qR¹², -(CH₂)_qR¹³ and -NR¹⁵R¹⁶; or is (C₁-C₇)alkyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkoxy, haloalkoxy, alkenyloxy, haloalkenyloxy, alkynyloxy, haloalkynyloxy, trialkylsilyl, cycloalkyl, -S(O)_nR¹³, -CN, -NO₂, -OH, -OR¹², -OR¹⁴, -COR¹⁵, -NR¹⁵COR¹⁶, -P(=O)(O-alkyl)₂, -P(=S)(O-alkyl)₂, -

$\text{NR}^{15}\text{SO}_2\text{R}^{13}$, $-\text{CONR}^{15}\text{R}^{16}$, $-\text{NR}^{15}\text{R}^{16}$, $-\text{S}(\text{O})_n\text{R}^{12}$, $-\text{S}(\text{O})_n\text{R}^{14}$, and $-\text{CO}_2\text{R}^{15}$; or R^5 and R^6 are taken together to form a ring selected from the following:



5

p is an integer selected from 0 or 1;

q is an integer selected from 0, 1, 2 and 3;

t is an integer selected from 0, 1 and 2;

10 R^{10} is alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl or halocycloalkyl;

R^{11} hydrogen, alkyl and haloalkyl;

R^{12} is phenyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, $-\text{CN}$, $-\text{NO}_2$, $-\text{S}(\text{O})_n\text{R}^{13}$, $-\text{COR}^{16}$, $-\text{COR}^{18}$, $-\text{CONR}^{15}\text{R}^{16}$, $-\text{SO}_2\text{NR}^{15}\text{R}^{16}$, $-\text{NR}^{15}\text{R}^{16}$, $-\text{OH}$, $-\text{SO}_3\text{H}$ and alkylideneimino;

15 R^{13} is haloalkyl, alkylcarbonyl or alkoxy carbonyl;

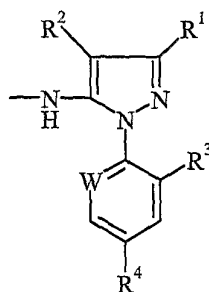
R^{14} is heterocyclyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, $-\text{CN}$, $-\text{NO}_2$, $-\text{S}(\text{O})_n\text{R}^{13}$, $-\text{OH}$ and $-\text{CO}_2\text{alkyl}$;

R^{15} and R^{17} are each independently hydrogen, alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl, cycloalkylalkyl, $-(CH_2)_qR^{18}$ or $-(CH_2)_qR^{14}$;

R^{16} and R^{19} are each independently hydrogen, alkyl, haloalkyl, cycloalkyl or cycloalkylalkyl;

5 R^{18} is phenyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, $-CN$, $-NO_2$, $-S(O)_nR^{13}$ and $-NR^{16}R^{19}$;

R^{20} and R^{21} are independently selected from hydrogen, alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl, cycloalkylalkyl, $-(CH_2)_qR^{18}$, $-(CH_2)_qR^{14}$, $-COalkyl$, $-S(O)_nalkyl$ or



(13);

R^{22} is hydrogen, alkyl, alkoxy, alkoxyalkyl, alkylthioalkyl or alkylsulfinylalkyl; and each heterocyclyl in the above-mentioned radicals is independently a heterocyclic

15 radical having 3 to 7 ring atoms and 1, 2 or 3 hetero atoms in the ring selected from the group consisting of N, O and S;

and

pesticidally acceptable salts thereof;

provided that when R^1 is cyano and R^2 is $-S(O)_nR^{10}$, then A and B are other than

20 methylene, X and Y are other than O and R^5 and R^6 are other than methyl.

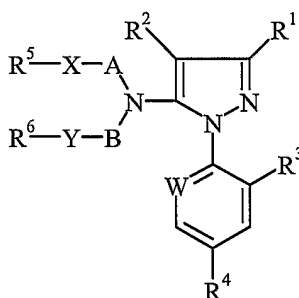
The present invention also includes compositions containing a pesticidally effective amount of at least one compound of formula I, and optionally, an effective amount of at least one additional compound, with at least one pesticidally compatible carrier.

25 The present invention also includes methods of controlling insects, general household pests and animal parasites in an area where control is desired, which comprise applying a pesticidally effective amount of the above composition to the

locus of crops, buildings, soil, animals or other areas where insects, general house hold pests or animal parasites are present or are expected to be present.

DETAILED DESCRIPTION OF THE INVENTION

5. The present invention generally relates to pesticidal compositions of 5-di-(substituted)aminopyrazole derivatives and to certain new and useful compounds, namely certain 5-di-(substituted)aminopyrazole derivatives that are surprisingly active in the control of insects, acarids, general household pests and domestic and non-domestic animal parasites when used in the pesticidal compositions and methods of this invention. The pesticidal compositions of the present invention are comprised of at least one of a pesticidally effective amount of a compound of formula I and at least one pesticidally compatible carrier therefor, wherein the compound of formula I is:



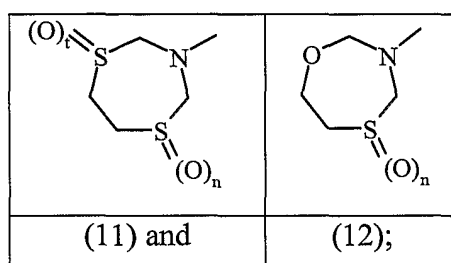
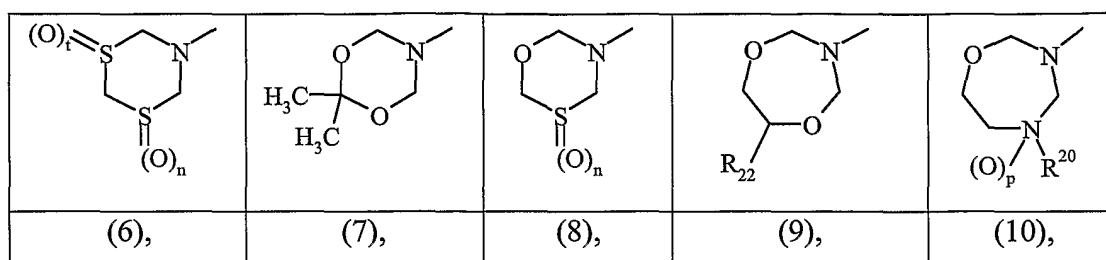
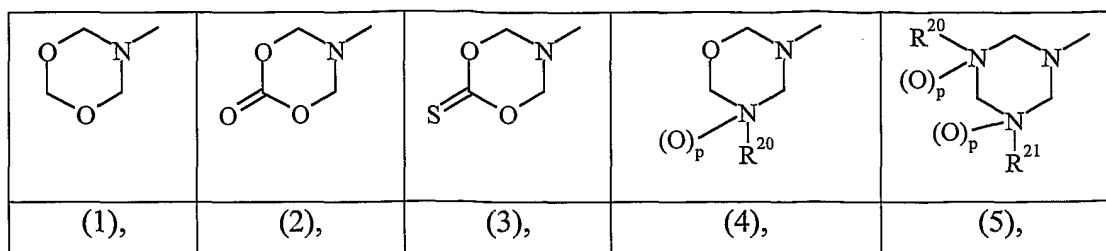
I

wherein

W is C-halogen, C-CH₃, C-CH₂F, C-CHF₂, C-CF₃, C-NO₂ or N;

- R¹ is selected from halogen, cyano, (C₁-C₄)alkyl, (C₁-C₄)haloalkyl, (C₃-C₆)cycloalkyl, -S(O)_nR¹⁰, formyl, acetyl, nitro, -C(S)NH₂, -C(=NNH₂)NH₂; or R¹ is -CR⁷=N-O-Y¹, wherein R⁷ is hydrogen, alkyl or R⁷ and Y¹ are taken together to form a 5 or 6 member ring or R⁷ is -NR⁸R⁹, wherein R⁸ and R⁹ are independently hydrogen or alkyl and Y¹ is hydrogen, alkenyl, alkynyl, formyl, alkylcarbonyl, cycloalkylcarbonyl, haloalkylcarbonyl, aroyl, arylalkylcarbonyl, alkylsulfonyl, arylsulfonyl, haloalkylcarbonyl, aminoalkylcarbonyl, alkylaminoalkylcarbonyl, dialkylaminocarbonyl, alkoxyalkylcarbonyl, arylalkoxycarbonyl, alkylthioalkylcarbonyl, alkylsulfonylalkylcarbonyl, arylthioalkoxycarbonyl, N-alkylcarbamoyl, N-arylcarbamoyl, N-alkylthiocarbamoyl, N-arylthiocarbamoyl, alpha-hydroxyarylalkylcarbonyl,

- hydroxyalkylcarbonyl, carboxyalkylcarbonyl, alkoxycarbonylalkylcarbonyl, -
 $P(=O)(O\text{-alkyl})_2$, $P(=S)(O\text{-alkyl})_2$, $P(=O)(S\text{-alkyl})_2$, trialkylsilyl,
 alkylcarbonylaminoalkylcarbonyl, alkylcarbonyloxyalkylcarbonyl, aryl,
 pyridinyl, pyrimidinyl, $-C(=O)S\text{-alkyl}$, $-C(=O)S\text{-aryl}$, $-C(=O)S\text{-alkylaryl}$,
 5 alkoxycarbonyl, alkylthioalkoxycarbonyl, alkylsulfonylalkoxycarbonyl,
 arylthioalkoxycarbonyl, alkoxycarbonyl, aryloxy carbonyl and
 aryloxy carbonylalkylcarbonyl; or alkyl or haloalkyl, optionally substituted by
 alkoxy, alkoxycarbonyl, carboxy, cyano, aminocarbonyl, alkylaminocarbonyl,
 dialkylaminocarbonyl, alkylthio, nitro, alkylsulfinyl, alkylsulfonyl,
 10 alkylcarbonyl, amino, alkylamino, dialkylamino, hydroxy, alkylcarbonylamino
 or alkylcarbonyloxy;
- R^2 is selected from hydrogen, halogen, $-S(O)_nR^{10}$, $(C_1\text{-}C_4)\text{alkyl}$, $(C_1\text{-}C_4)\text{haloalkyl}$,
 $(C_3\text{-}C_5)\text{alkenyl}$, $(C_3\text{-}C_5)\text{haloalkenyl}$, $(C_3\text{-}C_6)\text{cycloalkyl}$, $(C_3\text{-}C_6)\text{halocycloalkyl}$,
 $(C_3\text{-}C_5)\text{alkynyl}$, aryl, heteroaryl, $-NR^8R^9$, $-CO_2R^{15}$, $-CR^7=N-O-Y^1$, nitro or
 15 cyano;
- n is an integer selected from 0, 1 and 2;
- R^3 is hydrogen, halogen, cyano, formyl, acetyl, alkyl, haloalkyl or nitro;
- R^4 is halogen, $(C_1\text{-}C_4)\text{alkyl}$, $(C_1\text{-}C_4)\text{haloalkyl}$, $(C_3\text{-}C_5)\text{alkenyl}$, $(C_3\text{-}C_5)\text{alkynyl}$, $(C_1\text{-}C_4)\text{alkoxy}$, $(C_1\text{-}C_4)\text{haloalkoxy}$, $-S(O)_n\text{haloalkyl}$ or $-SF_5$;
- 20 A and B are independently selected from $(C_2\text{-}C_7)\text{alkylene}$ and haloalkylene ;
- X and Y are independently selected from O , $N-R^{11}$, $N(O)-R^{13}$, $SiR^{10}R^{10}$, and $S(O)_n$;
- R^5 and R^6 are independently selected from hydrogen, $(C_3\text{-}C_5)\text{alkenyl}$, $(C_3\text{-}C_5)\text{haloalkenyl}$, $(C_3\text{-}C_5)\text{alkynyl}$, $(C_3\text{-}C_5)\text{haloalkynyl}$, $(C_3\text{-}C_6)\text{cycloalkyl}$, -
 $(CH_2)_qR^{12}$, $-(CH_2)_qR^{13}$ and $-NR^{15}R^{16}$; or is $(C_1\text{-}C_7)\text{alkyl}$ unsubstituted or
 25 substituted by one or more radicals selected from the group consisting of
 halogen, alkoxy, haloalkoxy, alkenyloxy, haloalkenyloxy, alkynyloxy,
 haloalkynyloxy, trialkylsilyl, cycloalkyl, $-S(O)_nR^{13}$, $-CN$, $-NO_2$, $-OH$, $-OR^{12}$,
 $-OR^{14}$, $-COR^{15}$, $-NR^{15}COR^{16}$, $-P(=O)(O\text{-alkyl})_2$, $-P(=S)(O\text{-alkyl})_2$, $-NR^{15}SO_2R^{13}$,
 $-CONR^{15}R^{16}$, $-NR^{15}R^{16}$, $-S(O)_nR^{12}$, $-S(O)_nR^{14}$, and $-CO_2R^{15}$; or R^5 and R^6 are
 30 taken together to form a ring selected from the following:



p is an integer selected from 0 or 1;

5 q is an integer selected from 0, 1, 2 and 3;

t is an integer selected from 0, 1 and 2;

R¹⁰ is alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl or halocycloalkyl;

R¹¹ hydrogen, alkyl and haloalkyl;

10 R¹² is phenyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, -CN, -NO₂, -S(O)_nR¹³, -COR¹⁶, -COR¹⁸, -CONR¹⁵R¹⁶, -SO₂NR¹⁵R¹⁶, -NR¹⁵R¹⁶, -OH, -SO₃H and alkylideneimino;

R¹³ is haloalkyl, alkylcarbonyl or alkoxy carbonyl;

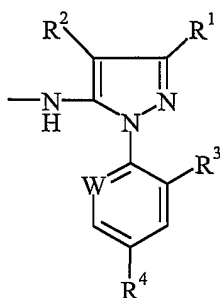
15 R¹⁴ is heterocyclyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, -CN, -NO₂, -S(O)_nR¹³, -OH and -CO₂alkyl;

R¹⁵ and R¹⁷ are each independently hydrogen, alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl, cycloalkylalkyl, -(CH₂)_qR¹⁸ or -(CH₂)_qR¹⁴;

R^{16} and R^{19} are each independently hydrogen, alkyl, haloalkyl, cycloalkyl or cycloalkylalkyl;

R^{18} is phenyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, -CN, -NO₂, -S(O)_nR¹³ and -NR¹⁶R¹⁹;

R^{20} and R^{21} are independently selected from hydrogen, alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl, cycloalkylalkyl, -(CH₂)_qR¹⁸, -(CH₂)_qR¹⁴, -COalkyl, -S(O)_nalkyl or



(13);

R^{22} is hydrogen, alkyl, alkoxy, alkoxyalkyl, alkylthioalkyl or alkylsulfinylalkyl; and each heterocyclyl in the above-mentioned radicals is independently a heterocyclic radical having 3 to 7 ring atoms and 1, 2 or 3 hetero atoms in the ring selected from the group consisting of N, O and S;

and

pesticidally acceptable salts thereof;

provided that when R^1 is cyano and R^2 is -S(O)_nR¹⁰, then A and B are other than methylene, X and Y are other than O and R^5 and R^6 are other than methyl.

Preferred 5-di-(substituted)aminopyrazole derivatives from the group set forth above are those where:

W is C-halogen;

R^1 is cyano;

R^2 is, -S(O)_nR¹⁰ or haloalkyl;

R^3 is halogen;

R^4 is haloalkyl;

A and B are each -CH₂-;

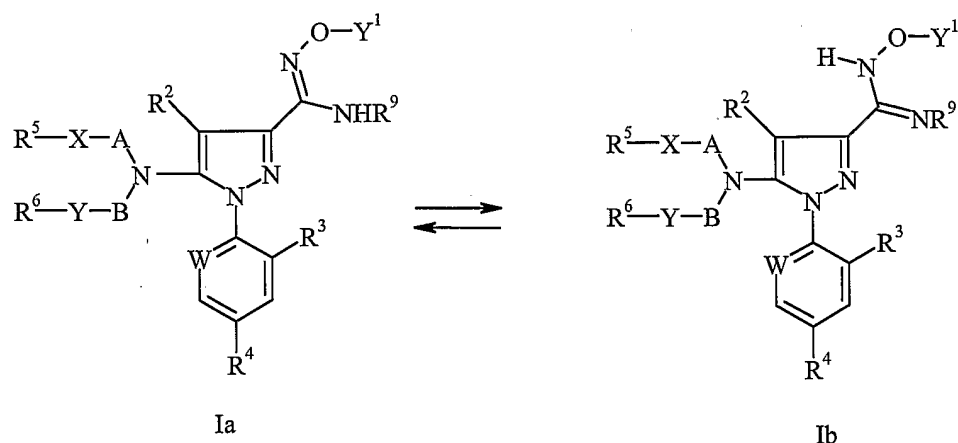
X and Y are each O or S(O)_n; and

R^5 and R^6 are each (C_1-C_6) alkyl or are taken together to form a ring of formula (9), formula (11) or formula (12).

More preferred 5-di-(substituted)aminopyrazole derivatives of the group set forth above are those where:

- 5 W is C-Cl;
- R^2 is, $-S(O)CF_3$ or CF_3 ;
- R^3 is chlorine;
- R^4 is CF_3 ;
- X and Y are each O or $S(O)_n$ where n is 0; and
- 10 R^5 and R^6 are each methyl or ethyl.

The compounds of the present invention may exist as tautomers, in which migration of a hydrogen atom within the molecule results in two or more structures, which are in equilibrium. For example, compounds of formula I wherein R^1 is - $CR^7=N-O-Y^1$, in which R^7 represents $-NR^8R^9$, in which R^8 represents hydrogen and R^9 represents hydrogen or alkyl may exist in tautomeric forms as shown in formulae Ia and Ib. Such tautomerism is well known as is described in S. Patai (The Chemistry of Functional Groups: Amidines and Imidates, Vol 2, 1991, pages 276-277). It will be understood that all such tautomeric forms are embraced by the present invention.



In addition, in certain cases the compounds of the present invention may possess asymmetric centers, which can give rise to optical enantiomorphs and diastereomers. The compounds may exist in two or more forms, i.e., polymorphs,

which are significantly different in physical and chemical properties. The compounds of the present invention may also possess acidic or basic moieties, which may allow for the formation of agriculturally acceptable salts or agriculturally acceptable metal complexes.

5 This invention includes the use of such enantiomorphs, polymorphs, tautomers, salts and metal complexes. Insecticidally acceptable salts and metal complexes include, without limitation, for example, ammonium salts, the salts of organic and inorganic acids, such as hydrochloric acid, sulfonic acid, ethanesulfonic acid, trifluoroacetic acid, methylbenzenesulfonic acid, phosphoric acid, gluconic
10 acid, pamoic acid, and other acid salts, and the alkali metal and alkaline earth metal complexes with, for example, sodium, potassium, lithium, magnesium, calcium, and other metals.

 The methods of the present invention comprise causing an insecticidally effective amount of a compound of formula I to be administered to insects in order
15 to kill or control the insects. Preferred insecticidally effective amounts are those that are sufficient to kill the insect. It is within the scope of the present invention to cause a compound of formula I to be present within insects by contacting the insects with a derivative of that compound, which derivative is converted within the insect to a compound of formula I. This invention includes the use of such compounds,
20 which are referred to as pro-insecticides.

 Another aspect of the present invention relates to compositions containing an insecticidally effective amount of at least one compound of formula I.

 Another aspect of the present invention relates to compositions containing an insecticidally effective amount of at least one compound of formula I, and an
25 effective amount of at least one additional compound.

 Another aspect of the present invention relates to methods of controlling insects by applying an insecticidally effective amount of a composition as set forth above to a locus of crops such as, without limitation, cereals, cotton, vegetables, and fruits, or other areas where insects are present or are expected to be present.

30 The present invention also includes the use of the compounds and compositions set forth herein for control of non-agricultural insect species, for example, dry wood termites and subterranean termites; as well as for use as pharmaceutical agents. In the field of veterinary medicine, the compounds of the

present invention are expected to be effective, orally, parenterally and topically, against certain *endo*- and *ecto*-parasites, such as insects and worms, which prey on animals. Examples of such animal parasites include, without limitation, *Gastrophilus* spp., *Stomoxys* spp., *Trichodectes* spp., *Rhodnius* spp.,

5 Ctenocephalides canis, and other species.

The compounds of the present invention are generally more efficacious or have a reduced insect resistance factor or have a broader spectrum of activity or are safer (e.g. less toxic to mammals) or have other more advantageous properties than the compounds of the prior art.

10 As used in this specification and unless otherwise indicated the substituent terms "alkyl" and "alkoxy", used alone or as part of a larger moiety, includes straight or branched chains of at least one or two carbon atoms, as appropriate to the substituent, and preferably up to 12 carbon atoms, more preferably up to ten carbon atoms, most preferably up to seven carbon atoms. The term "alkylene" is to be
15 understood as meaning a straight or branched saturated carbon chain having from 1 to 12 atoms. The term "haloalkylene" is to be understood as meaning a straight or branched saturated carbon chain having from 1 to 12 atoms, in which one or more hydrogen atoms are replaced by the same number of halogen atoms. The terms "haloalkyl" and "haloalkoxy" used alone or as part of a larger moiety, includes
20 straight or branched chains of at least one or two carbon atoms, as appropriate to the substituent, and preferably up to 12 carbon atoms, more preferably up to ten carbon atoms, most preferably up to seven carbon atoms, wherein one or more hydrogen atoms have been replaced with halogen atoms, for example, trifluoromethyl or 2,2,2-trifluoroethoxy. The term "alkenyl" and "alkynyl" used alone or as part of a larger
25 moiety, includes straight or branched chains of at least two carbon atoms containing at least one carbon-carbon double bond or triple bond, and preferably up to 12 carbon atoms, more preferably up to ten carbon atoms, most preferably up to seven carbon atoms. The term "aroyl" designates a carbonyl aromatic radical, that is, aryl-C(O)-, which is preferably a benzoyl optionally substituted by one or more alkyl, alkoxy or halogen groups. The term "aryl" refers to an aromatic ring structure,
30 including fused rings, having six to ten carbon atoms, for example, phenyl, indanyl, indenyl, naphthyl or 5,6,7,8-tetrahydronaphthyl. The term "heteroaryl" refers to an aromatic ring structure, including fused rings, in which at least one of the atoms is

other than carbon, for example, without limitation, sulfur, oxygen, or nitrogen. Heteroaryl rings include, without limitation, for example, oxazolyl, thiazolyl, imidazolyl, pyrazolyl, triazolyl or thiadiazolyl. The term "DMF" refers to N,N-dimethylformamide. The term "THF" refers to tetrahydrofuran. The term

5 "halogen" or "halo" refers to fluorine, bromine, iodine, or chlorine. The term "ambient temperature", for example, in reference to a chemical reaction mixture temperature, refers to a temperature in the range of 20 °C to 30 °C. The term "insecticidal" or "acaricidal", "insecticide" or "acaricide" refers to a compound of

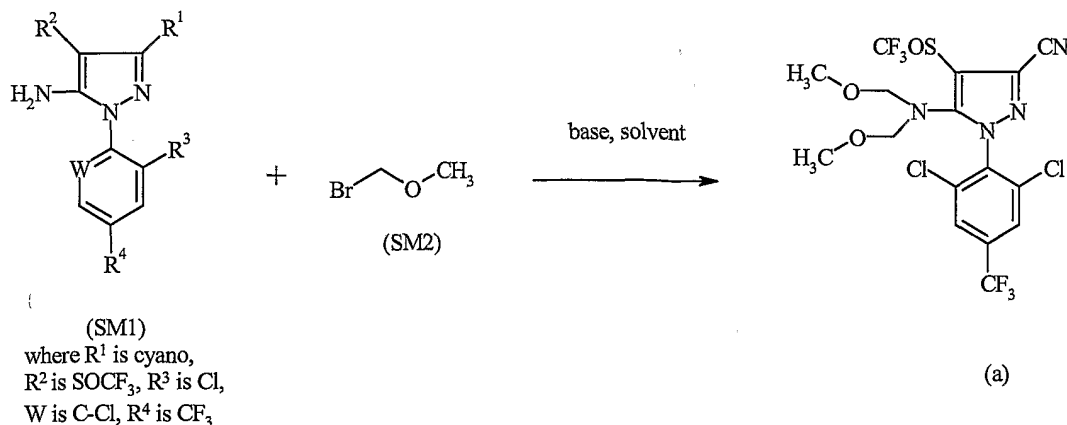
10 the present invention, either alone or in admixture with at least one additional compound, or with at least one compatible carrier, which causes the destruction or the inhibition of action of insects or acarids. The term "independently selected from" as set forth above and in the claims section of the present specification refers to the possibility that moieties, for example the R⁵ and R⁶, may be the same or they may be different within the group that the selection is made. The term "general

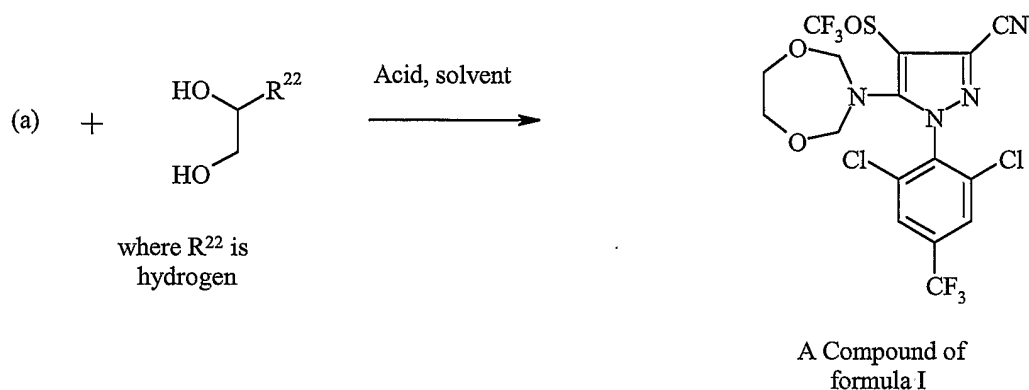
15 household pest" refers to any insect or pest, such as German cockroach, American cockroach, Smokey-Brown cockroach, Oriental cockroach, house fly, biting fly, filth fly, red imported fire ant (RIFA), odorous house ant, carpenter ant, pharaoh ant, termite, Argentine ant, mosquito, tick, flea, sowbug, pillbug, centipede, spider, silverfish, scorpion and bed bug, that cause harm or nuisance to person or property.

20 The 5-di-(substituted)aminopyrazole derivatives of formula I can be synthesized by methods that are individually known to one skilled in the art from available intermediate compounds. A number of the compounds of the present invention were prepared in the manner shown in Scheme 1.

Scheme 1

25

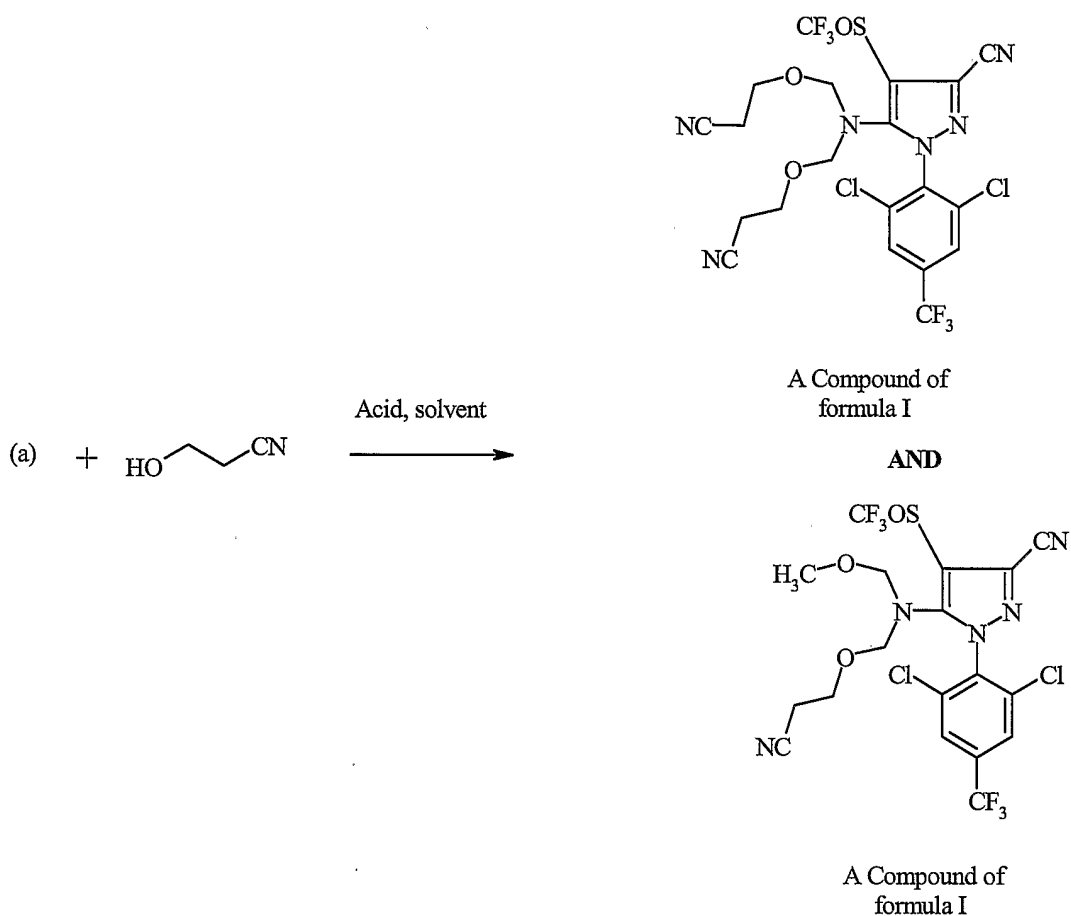




As depicted in Scheme 1, the reaction of an appropriately substituted 1-arylpyrazole(SM1) (known compound) and an excess of a halogenated alkyl alkyl ether, for example, bromomethyl methyl ether (SM2) yielded the appropriate di(substituted-alkyl)aminopyrazole intermediate (a), for example, 3-cyano-1-(2,6-dichloro-4-trifluoromethyl)phenyl-5-bis(methoxymethyl)amino-4-(trifluoromethylsulfinyl)pyrazole. The reaction of intermediate (a) with an appropriately substituted alcohol, for example, ethylene glycol, yielded the correspondingly substituted pyrazole, for example, 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-(1,5,3-dioxazaperhydroepin-3-yl)-4-(trifluoromethylsulfinyl)pyrazole-3-carbonitrile, a compound of formula I, described in detail in Example 1 set forth below.

Another method for the production of compounds of formula I is shown in Scheme 2.

Scheme 2

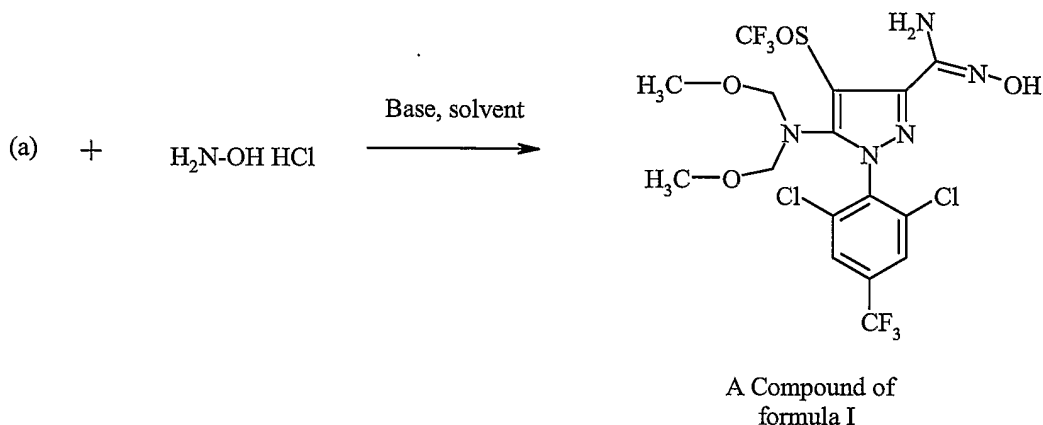


The reaction of intermediate (a) with an appropriately substituted alcohol, for
 5 example, 3-hydroxypropionitrile, yielded the substituted pyrazole compounds where
 1) R^5 and R^6 are both cyanoethyl and 2) R^5 is methyl and R^6 is cyanoethyl, for
 example, 1) 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-{bis[(2-
 cyanoethoxy)methyl]amino}-4-(trifluoromethylsulfinyl)pyrazole-3-carbonitrile and
 2) 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-[[2-
 10 cyanoethoxy)methyl](methoxymethyl)amino}-4-(trifluoromethylsulfinyl)pyrazole-
 3-carbonitrile, compounds of formula I, described in detail in Example 2 set forth
 below.

A general method for the preparation of compounds of the present invention
 where the R^1 group is other than cyano is shown in Scheme 3.

15

Scheme 3



The reaction of intermediate (a) with hydroxylamine hydrochloride under
 5 basic conditions yielded 3-(amino(hydroxyimino)methyl)-1-(2,6-dichloro-4-
 trifluoromethylphenyl)-5-[bis(methoxymethyl)amino]-4-
 (trifluoromethylsulfinyl)pyrazole, a compound of formula I described in detail in
 Example 3 set forth below.

One skilled in the art will, of course, recognize that the formulation and
 10 mode of application of a toxicant may affect the activity of the material in a given
 application. Thus, for agricultural and general household pest use the present
 insecticidal compounds may be formulated as a granular of relatively large particle
 size (for example, 8/16 or 4/8 US Mesh), as water-soluble or water-dispersible
 granules, as powdery dusts, as wettable powders, as emulsifiable concentrates, as
 15 aqueous emulsions, as solutions, or as any of other known types of useful
 formulations, depending on the desired mode of application. It is to be understood
 that the amounts specified in this specification are intended to be approximate only,
 as if the word "about" were placed in front of the amounts specified.

These insecticidal compositions may be applied either as water-diluted
 20 sprays, or dusts, or granules to the areas in which suppression of insects is desired.
 These formulations may contain as little as 0.1%, 0.2% or 0.5% to as much as 95%
 or more by weight of active ingredient.

Dusts are free flowing admixtures of the active ingredient with finely divided
 solids such as talc, natural clays, kieselguhr, flours such as walnut shell and
 25 cottonseed flours, and other organic and inorganic solids which act as dispersants
 and carriers for the toxicant; these finely divided solids have an average particle size

of less than about 50 microns. A typical dust formulation useful herein is one containing 1.0 part or less of the insecticidal compound and 99.0 parts of talc.

Wettable powders, also useful formulations for insecticides, are in the form of finely divided particles that disperse readily in water or other dispersant. The wettable powder is ultimately applied to the locus where insect control is needed either as a dry dust or as an emulsion in water or other liquid. Typical carriers for wettable powders include Fuller's earth, kaolin clays, silicas, and other highly absorbent, readily wet inorganic diluents. Wettable powders normally are prepared to contain about 5-80% of active ingredient, depending on the absorbency of the carrier, and usually also contain a small amount of a wetting, dispersing or emulsifying agent to facilitate dispersion. For example, a useful wettable powder formulation contains 80.0 parts of the insecticidal compound, 17.9 parts of Palmetto clay, and 1.0 part of sodium lignosulfonate and 0.3 part of sulfonated aliphatic polyester as wetting agents. Additional wetting agent and/or oil will frequently be added to a tank mix for to facilitate dispersion on the foliage of the plant.

Other useful formulations for insecticidal applications are emulsifiable concentrates (ECs) which are homogeneous liquid compositions dispersible in water or other dispersant, and may consist entirely of the insecticidal compound and a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone, or other non-volatile organic solvents. For insecticidal application these concentrates are dispersed in water or other liquid carrier and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises 0.5 to 95% of active ingredient by weight of the insecticidal composition.

Flowable formulations are similar to ECs, except that the active ingredient is suspended in a liquid carrier, generally water. Flowables, like ECs, may include a small amount of a surfactant, and will typically contain active ingredients in the range of 0.5 to 95%, frequently from 10 to 50%, by weight of the composition. For application, flowables may be diluted in water or other liquid vehicle, and are normally applied as a spray to the area to be treated.

Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, but are not limited to, the alkyl and alkylaryl sulfonates and

sulfates and their sodium salts; alkylaryl polyether alcohols; sulfated higher alcohols; polyethylene oxides; sulfonated animal and vegetable oils; sulfonated petroleum oils; fatty acid esters of polyhydric alcohols and the ethylene oxide addition products of such esters; and the addition product of long-chain mercaptans and ethylene oxide. Many other types of useful surface-active agents are available in commerce. Surface-active agents, when used, normally comprise 1 to 15% by weight of the composition.

Other useful formulations include suspensions of the active ingredient in a relatively non-volatile solvent such as water, corn oil, kerosene, propylene glycol, or other suitable solvents.

Still other useful formulations for insecticidal applications include simple solutions of the active ingredient in a solvent in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene, or other organic solvents. Granular formulations, wherein the toxicant is carried on relative coarse particles, are of particular utility for aerial distribution or for penetration of cover crop canopy. Pressurized sprays, typically aerosols wherein the active ingredient is dispersed in finely divided form as a result of vaporization of a low-boiling dispersant solvent carrier may also be used. Water-soluble or water-dispersible granules are free flowing, non-dusty, and readily water-soluble or water-miscible. In use by the farmer on the field, the granular formulations, emulsifiable concentrates, flowable concentrates, aqueous emulsions, solutions, etc., may be diluted with water to give a concentration of active ingredient in the range of say 0.1% or 0.2% to 1.5% or 2%.

The active insecticidal compounds of this invention may be formulated and/or applied with one or more additional compound. Such combinations may provide certain advantages, such as, without limitation, exhibiting synergistic effects for greater control of insect pests, reducing rates of application of insecticide thereby minimizing any impact to the environment and to worker safety, controlling a broader spectrum of insect pests, safening of crop plants to phytotoxicity, and improving tolerance by non-pest species, such as mammals and fish.

Additional compounds include, without limitation, other pesticides, plant growth regulators, fertilizers, soil conditioners, or other agricultural chemicals. In applying an active compound of this invention, whether formulated alone or with

other agricultural chemicals, an effective amount and concentration of the active compound is of course employed; the amount may vary in the range of, e.g. about 0.001 to about 3 kg/ha, preferably about 0.03 to about 1 kg/ha. For field use, where there are losses of insecticide, higher application rates (e.g., four times the rates
5 mentioned above) may be employed.

When the active insecticidal compounds of the present invention are used in combination with at least one additional compound, e.g., with other pesticides such as herbicides, the herbicides include, without limitation, for example: N-(phosphonomethyl)glycines such as glyphosate; aryloxyalkanoic acids such as 2,4-D, MCPA, and MCPP; ureas such as isoproturon; imidazolinones such as imazapyr,
10 D, MCPA, and MCPP; ureas such as isoproturon; imidazolinones such as imazapyr, imazamethabenz, imazethapyr, and imazaquin; diphenyl ethers such as acifluorfen, bifenox, and fomasafen; hydroxybenzonitriles such as ioxynil and bromoxynil; sulfonylureas such as chlorimuron, achlorsulfuron, bensulfuron, pyrazosulfuron, thifensulfuron, and triasulfuron; 2-(4-aryloxyphenoxy)alkanoic acids such as
15 fenoxaprop, fluazifop, quizalofop, and diclofop; benzothiadiazinones such as bentazone; 2-chloroacetanilides such as butachlor, metolachlor, acetochlor, and dimethenamide; arenecarboxylic acids such as dicamba; pyridyloxyacetic acids such as fluroxypyr, aryl triazolinones such as sulfentrazone and carfentrazone-ethyl; isoxazolidinones such as clomazone; and other herbicides.

When the active insecticidal compounds of the present invention are used in combination with at least one additional compound, e.g., with other pesticides such as other insecticides, the other insecticides include, for example: organophosphate insecticides, such as chlorpyrifos, diazinon, dimethoate, malathion, parathion-methyl, and terbufos; pyrethroid insecticides, such as fenvalerate, deltamethrin,
25 fenpropathrin, cyfluthrin, flucythrinate, *alpha*-cypermethrin, *beta*-cypermethrin, *zeta*-cypermethrin, bifenthrin, cypermethrin, permethrin, resolved cyhalothrin, etofenprox, esfenvalerate, tralomehtrine, tefluthrin, cycloprothrin, betacyfluthrin, and acrinathrin; carbamate insecticides, such as aldecarb, carbaryl, carbofuran, and methomyl; organochlorine insecticides, such as endosulfan, endrin, heptachlor, and
30 lindane; benzoylurea insecticides, such as diflubenzuron, triflumuron, teflubenzuron, chlorfluazuron, flucycloxuron, hexaflumuron, flufenoxuron, and lufenuron; and other insecticides, such as amitraz, clofentezine, fenpyroximate, hexythiazox, spinosad, imidacloprid, and other insecticides.

When the active insecticidal compounds of the present invention are used in combination with one or more of an additional compound, e.g., with other pesticides such as fungicides, the fungicides include, for example: benzimidazole fungicides, such as benomyl, carbendazim, thiabendazole, and thiophanate-methyl; 1,2,4-
5 triazole fungicides, such as epoxyconazole, cyproconazole, flusilazole, flutriafol, propiconazole, simeconazole, tebuconazole, triadimefon, and triadimenol; substituted anilide fungicides, such as metalaxyl, oxadixyl, procymidone, and vinclozolin; organophosphorus fungicides, such as fosetyl, iprobenfos, pyrazophos, edifenphos, and tolclofos-methyl; morpholine fungicides, such as fenpropimorph,
10 tridemorph, and dodemorph; other systemic fungicides, such as fenarimol, imazalil, prochloraz, tricyclazole, and triforine; dithiocarbamate fungicides, such as mancozeb, maneb, propineb, zineb, and ziram; non-systemic fungicides, such as chlorothalonil, dichlofluanid, dithianon, and iprodione, captan, dinocap, dodine, fluazinam, gluzatine, PCNB, pencycuron, quintozone, tricylamide, and
15 validamycin; inorganic fungicides, such as copper and sulphur products, and other fungicides.

When the active insecticidal compounds of the present invention are used in combination with at least one additional compound, e.g., with other pesticides such as nematocides, the nematocides include, for example: carbofuran, carbosulfan,
20 terbufos, aldecarb, ethoprop, fenamphos, oxamyl, isazofos, cadusafos, and other nematocides.

When the active insecticidal compounds of the present invention are used in combination with one or more of an additional compound, e.g., with other materials such as plant growth regulators, the plant growth regulators include, for example:
25 maleic hydrazide, chlormequat, ethephon, gibberellin, mepiquat, thidiazon, inabenfide, triaphenthenol, paclobutrazol, uniconazole, DCPA, prohexadione, trinexapac-ethyl, and other plant growth regulators.

Soil conditioners are materials which, when added to the soil, promote a variety of benefits for the efficacious growth of plants. Soil conditioners are used to
30 reduce soil compaction, promote and increase effectiveness of drainage, improve soil permeability, promote optimum plant nutrient content in the soil, and promote better pesticide and fertilizer incorporation. When the active insecticidal compounds of the present invention are used in combination with one or more of second

compounds, e.g., with other materials such as soil conditioners, the soil conditioners include organic matter, such as humus, which promotes retention of cation plant nutrients in the soil; mixtures of cation nutrients, such as calcium, magnesium, potash, sodium, and hydrogen complexes; or microorganism compositions which
5 promote conditions in the soil favorable to plant growth. Such microorganism compositions include, for example, *bacillus*, *pseudomonas*, *azotobacter*, *azospirillum*, *rhizobium*, and soil-borne *cyanobacteria*.

Fertilizers are plant food supplements, which commonly contain nitrogen, phosphorus, and potassium. When the active insecticidal compounds of the present
10 invention are used in combination with one or more of second compounds, e.g., with other materials such as fertilizers, the fertilizers include nitrogen fertilizers, such as ammonium sulfate, ammonium nitrate, and bone meal; phosphate fertilizers, such as superphosphate, triple superphosphate, ammonium sulfate, and diammonium sulfate; and potassium fertilizers, such as muriate of potash, potassium sulfate, and
15 potassium nitrate, and other fertilizers.

For veterinary use of the compounds of the present invention in domestic and non-domestic animals, the compounds may be administered alone or in a formulation appropriate to the specific use envisaged and to the particular species of host animal being treated and the parasite involved. The methods by which the
20 compounds may be administered include oral administration by capsule, bolus, tablet or drench, or as a pour-on or spot-on formulation, or alternatively, they can be administered by injection (e.g. subcutaneously, intramuscularly or intravenously), dip, spray, mousse, shampoo, powder, or as an implant.

Such formulations are prepared in a conventional manner in accordance with
25 standard veterinary practice. Thus capsules, boluses or tablets may be prepared by mixing the active ingredient with a suitable finely divided diluent or carrier additionally containing a disintegrating agent and/or binder such as starch, lactose, talc, magnesium stearate etc. Oral drenches are prepared by dissolving or suspending the active ingredient in a suitable medium. Injectable formulations may
30 be prepared in the form of a sterile solution which may contain other substances, for example, enough salts or glucose to make the solution isotonic with blood. Acceptable liquid carriers include the vegetable oils such as sesame oil and the like, glycerides such as triacetin and the like, esters such as benzyl benzoate, isopropyl

myristate and fatty acid derivatives of propylene glycol and the like, as well as organic solvents such as pyrrolidone, glycerol formal and the like. The formulations are prepared by dissolving or suspending the active ingredient in the liquid carrier such that the final formulation contains from 0.01 to 10% by weight of the active
5 ingredient.

These formulations will vary with regard to the weight of active compound contained therein depending on the species of host animal to be treated, the severity and type of infection and the body weight of the host. For parenteral, topical (e.g. using pour-on or spot-on, dip, spray, mousse, shampoo or powder to deliver the
10 compound) and oral administration, typical dose ranges of the active ingredient are 0.01-100 mg per kg of body weight of the animal. Preferably the range is 0.1 to 10 mg per kg.

As an alternative the compounds may be administered with the animal feedstuff and for this purpose a concentrated feed additive or premix may be
15 prepared for mixing with the normal animal feed.

The compounds of the invention may, in particular, be used in the field of veterinary medicine and livestock husbandry against arthropods, helminths or protozoa which are parasitic internally or externally upon vertebrates, particularly warm-blooded vertebrates, for example domestic and non-domestic animals, e.g.
20 cattle, sheep, goats, equines, swine, poultry, dogs, and cats. The compounds of the invention are particularly useful in controlling arthropods, helminths or protozoa which are present inside the host animals or which feed in or on the skin or suck the blood of the animal, for which purpose they may be administered orally, parenterally, percutaneously or topically.

25 According to a further aspect of the invention, there is provided a pesticidal formulation comprising a compound of the invention, in admixture with a compatible adjuvant, diluent or carrier. Preferably, the formulation is adapted for topical administration.

The invention further provides a compound of the invention for use as a
30 pesticide; and a method of treating a pest infestation at a locus, which comprises treatment of the locus with an effective amount of a compound of the invention. Preferably, the locus is the skin or fur of an animal.

The following examples further illustrate the present invention, but, of course, should not be construed as in any way limiting its scope. The examples are organized to present protocols for the synthesis of the compounds of formula I of the present invention, set forth a list of such synthesized species, and set forth certain biological data indicating the efficacy of such compounds.

EXAMPLE 1

This example illustrates one protocol for the preparation of 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-(1,5,3-dioxazaperhydroepin-3-yl)-4-(trifluoromethylsulfinyl)-pyrazole-3-carbonitrile
(Compound 3-10)

Step A 3-cyano-1-(2,6-dichloro-4-trifluoromethyl)phenyl-5-bis(methoxymethyl)amino-4-(trifluoromethylsulfinyl)pyrazole as an intermediate

Under a dry nitrogen atmosphere a solution of 1.0 gram (0.0023 mole) of 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethyl)phenyl-4-(trifluoromethylsulfinyl)pyrazole (known compound, U.S. Patent 5,232,940) in 10 mL of THF was added to a stirred, cold (0°C) mixture of 0.2 gram (0.005 mole) of a 60% sodium hydride suspension in mineral oil in 10 mL of THF. The cold reaction mixture was stirred for 10 minutes and 0.61 gram (0.005 mole) of bromomethyl methyl ether was added. The cold reaction mixture was stirred for 3 hours. The reaction mixture was diluted with ethyl acetate, washed in succession with an aqueous saturated ammonium chloride solution, an aqueous saturated sodium bicarbonate solution and an aqueous saturated sodium chloride solution, and then dried with magnesium sulfate. The solution was filtered and the filtrate was concentrated under reduced pressure leaving an oil. The oil was dissolved in about 10 mL of diethyl ether to which n-heptane was added slowly, forming a white solid. The solid was isolated and dried under reduced pressure, yielding 0.81 gram of the subject compound. The NMR spectrum was consistent with the proposed structure.

Step B 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-(1,5,3-dioxazaperhydroepin-3-yl)-4-(trifluoromethylsulfinyl)-pyrazole-3-carbonitrile (Compound 3-10)

Under a dry nitrogen atmosphere a mixture of 0.28 gram (0.00053 mole) of 3-cyano-1-(2,6-dichloro-4-trifluoromethyl)phenyl-5-bis(methoxymethyl)amino-4-(trifluoromethylsulfinyl)pyrazole, 0.34 gram (0.0054 mole) of ethylene glycol and 0.1 mL of a 4M solution of hydrochloric acid in 1,4-dioxane was stirred in 10 mL of acetonitrile at ambient temperature for about 18 hours. The reaction mixture was concentrated under reduced pressure leaving a residue. The residue was purified by column chromatography on silica gel, eluting with mixtures of ethyl acetate in hexanes. The appropriate fractions were combined and concentrated under reduced pressure, yielding 0.09 gram of the title compound as a solid. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 2

This example illustrates one protocol for the preparation of 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-[[(2-cyanoethoxy)methyl](methoxymethyl)amino]-4-(trifluoromethylsulfinyl)pyrazole-3-carbonitrile (Compound 1-58) and 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-{bis[(2-cyanoethoxy)methyl]amino}-4-(trifluoromethylsulfinyl)pyrazole-3-carbonitrile (Compound 1-47)

Under a dry nitrogen atmosphere a mixture of 0.2 gram (0.00038 mole) of 3-cyano-1-(2,6-dichloro-4-trifluoromethyl)phenyl-5-bis(methoxymethyl)amino-4-(trifluoromethylsulfinyl)pyrazole, 0.27 gram (0.00038 mole) of 3-hydroxypropionitrile and 0.1 mL of a 4M solution of hydrochloric acid in 1,4-dioxane was stirred in 10 mL of acetonitrile at ambient temperature for about 18 hours. The reaction mixture was concentrated under reduced pressure leaving a residue. The residue was purified by column chromatography on silica gel, eluting with mixtures of ethyl acetate in hexanes, providing two products. The appropriate fractions of the first product to elute were combined and concentrated under reduced pressure, yielding 0.34 gram of a residue. Analysis of the residue by NMR indicated a quantity of 3-hydroxypropionitrile was present. The residue was dissolved in methylene chloride, washed with two portions of water then concentrated under reduced pressure to yield 0.1 gram of 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-[[(2-cyanoethoxy)methyl](methoxymethyl)amino]-4-(trifluoromethylsulfinyl)pyrazole-3-carbonitrile (Compound 1-58) as an oil. The appropriate fractions of the second product to elute were combined and concentrated

under reduced pressure yielding 0.045 gram of 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-{bis[(2-cyanoethoxy)methyl]amino}-4-(trifluoromethylsulfinyl)pyrazole-3-carbonitrile (Compound 1-47) as an oil. The NMR spectra were consistent with the proposed structures.

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EXAMPLE 3

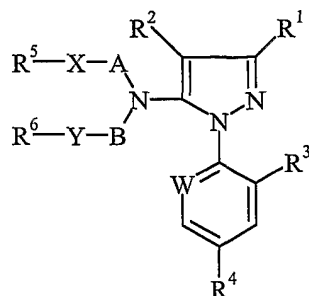
This example illustrates one protocol for the preparation of 3-(amino(hydroxyimino)methyl)-1-(2,6-dichloro-4-trifluoromethylphenyl)-5-[bis(methoxymethyl)amino]-4-(trifluoromethylsulfinyl)pyrazole (Compound 1-5)

10 A mixture of 0.21 gram (0.0004 mole) of 3-cyano-1-(2,6-dichloro-4-trifluoromethyl)phenyl-5-bis(methoxymethyl)amino-4-(trifluoromethylsulfinyl)pyrazole, 0.028 gram (0.0004 mole) of hydroxylamine hydrochloride and 0.05 gram (0.00046 mole) of triethylamine in 10.0 mL of methanol was stirred at ambient temperature in a sealed reaction vial for about 18
15 hours. The reaction mixture was concentrated under reduced pressure leaving a residue. The residue was partitioned between ethyl acetate and water. The organic phase was washed with an aqueous saturated sodium chloride solution, dried with magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure to a residue. The residue was purified by column chromatography on silica
20 gel, eluting with mixtures of ethyl acetate and hexanes. The appropriate fractions were combined and concentrated under reduced pressure to yield 0.1 gram of the title compound as a solid. The NMR spectrum was consistent with the proposed structure.

It is well known to one of ordinary skill in the art that compounds like the
25 compounds of formula I of the present invention can contain optically active and racemic forms. It is also well known in the art that compounds like the compounds of formula I may contain stereoisomeric forms, tautomeric forms and/or exhibit polymorphism. It is to be understood that the present invention encompasses any racemic, optically active, polymorphic, tautomeric, or stereoisomeric form, or
30 mixtures thereof. It should be noted that it is well known in the art how to prepare optically active forms, for example by resolution of a racemic mixture, or by synthesis from optically active intermediates.

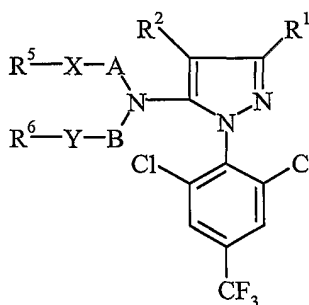
The following table sets forth some compounds of formula I:

Table 1
5-Di-(substituted-alkyl)aminopyrazole derivatives



I

compounds of formula I where R³ is chlorine, R⁴ is -CF₃, W is C-Cl providing the following compounds:



I-1

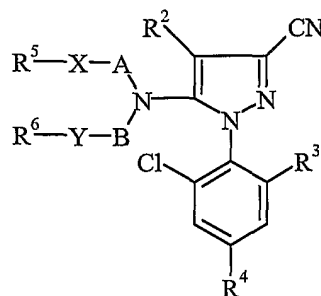
Cmpd. No	R ¹	R ²	-A-X-R ⁵	-B-Y-R ⁶
1-1	-CN	-SOCF ₃	-CH ₂ SCH ₂ CH ₂ OH	-CH ₂ SCH ₂ CH ₂ OH
1-2	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₅	-CH ₂ OC ₂ H ₅
1-3	-CN	-CF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-4	-CN	-SOCF ₃	-CH ₂ SOC ₂ H ₅	-CH ₂ SOC ₂ H ₅
1-5	-C(NO ₂)NH ₂	-SOCF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-6	-CN	-SOCF ₃	-CH ₂ SCH ₂ Ph	-CH ₂ SCH ₂ Ph
1-7	-CN	-SOCF ₃	-CH ₂ OCH ₂ Ph	-CH ₂ OCH ₂ Ph
1-8	-CN	-SOCF ₃	-CH ₂ OCH ₂ CH=CH ₂	-CH ₂ OCH ₂ CH=CH ₂
1-9	-CHO	-SOCF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-10	-COCH ₃	-SOCF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-11	-Cl	-SOCF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-12	-C(NOCH ₃)H	-SOCF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-13	-CSNH ₂	-SOCF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-14	-CHO	-SOCHF ₂	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-15	-COCH ₃	-SOCHF ₂	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-16	-C(NOCH ₃)H	-SOCHF ₂	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-17	-CSNH ₂	-SOCH ₂ F	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-18	-CHO	-SOCH ₂ F	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-19	-CSNH ₂	-SOCH ₂ F	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-20	-CHO	-SOCH ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-21	-COCH ₃	-SOCH ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-22	-C(NOCH ₃)H	-SOCH ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-23	-NO ₂	-SOCF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-24	-CN	-SOCF ₃	-C ₂ H ₄ OCH ₃	-CH ₂ OCH ₃
1-25	-CN	-SOCH ₃	-C ₂ H ₄ OCH ₃	-CH ₂ OCH ₃

Cmpd. No	R ¹	R ²	-A-X-R ⁵	-B-Y-R ⁶
1-26	-CN	-SOC ₂ H ₅	-C ₂ H ₄ OCH ₃	-CH ₂ OCH ₃
1-27	-CN	-SOCF ₃	-C ₂ H ₄ OCH ₃	-C ₂ H ₄ OCH ₃
1-28	-CN	-SOCF ₃	-C ₂ H ₄ OCH ₃	-CH ₂ OCH ₃
1-29	-CN	-SOCH ₃	-C ₂ H ₄ OCH ₃	-CH ₂ OCH ₃
1-30	-CN	-SOC ₂ H ₅	-C ₂ H ₄ OCH ₃	-CH ₂ OCH ₃
1-31	-CN	-SOCHF ₂	-C ₂ H ₄ OCH ₃	-C ₂ H ₄ OCH ₃
1-32	-CN	-SOCF ₃	-C ₂ H ₄ NHCH ₃	-CH ₂ OCH ₃
1-33	-CN	-SOCF ₃	-C ₂ H ₄ NHCH ₃	-CH ₂ SCH ₃
1-34	-CN	-SOCF ₃	-C ₂ H ₄ SO ₂ CH ₃	-CH ₂ OCH ₃
1-35	-CN	-SOCF ₃	-C ₂ H ₄ NO(CH ₃) ₂	-CH ₂ OCH ₃
1-36	-CN	-SOCF ₃	-CH ₂ SCH ₃	-CH ₂ SCH ₃
1-37	-CN	-SOCF ₃	-CH ₂ OSOCH ₃	-CH ₂ OSOCH ₃
1-38	-CN	-SOCF ₃	-CH ₂ SCH ₃	-CH ₂ OCH ₃
1-39	-CN	-SOCF ₃	-CH ₂ N(CH ₃) ₂	-CH ₂ OCH ₃
1-40	-CN	-SOCF ₃	-CH ₂ N(CH ₃) ₂	-CH ₂ N(CH ₃) ₂
1-41	-CN	-SOCF ₃	-CH ₂ OCOCH ₃	-CH ₂ OCOCH ₃
1-42	-CN	-SOCF ₃	-CH ₂ NCOCH ₃	-CH ₂ NCOCH ₃
1-43	-CN	-SOCF ₃	-CH ₂ OSO ₂ CH ₃	-CH ₂ OSO ₂ CH ₃
1-44	-CN	-SOCF ₃	-CH ₂ NSO ₂ CH ₃	-CH ₂ NSO ₂ CH ₃
1-45	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ OCH ₃	-CH ₂ OC ₂ H ₄ OCH ₃
1-46	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ Si(CH ₃) ₃	-CH ₂ OC ₂ H ₄ Si(CH ₃) ₃
1-47	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ CN	-CH ₂ OC ₂ H ₄ CN
1-48	-CN	*-SOCF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-49	-CN	** -SOCF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
1-50	-CN	*-SOCF ₃	-CH ₂ SCH ₃	-CH ₂ SCH ₃
1-51	-CN	** -SOCF ₃	-CH ₂ SCH ₃	-CH ₂ SCH ₃
1-52	-CN	-SOCF ₃	-CH ₂ OPO(OCH ₃) ₂	-CH ₂ OPO(OCH ₃) ₂
1-53	-CN	-SOCF ₃	-C ₂ H ₄ N(CH ₃) ₂	-CH ₂ OCH ₃
1-54	-CN	-SOCF ₃	-CH ₂ SC ₂ H ₄ OPh	-CH ₂ SC ₂ H ₄ OPh
1-55	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ SCH ₃	-CH ₂ OC ₂ H ₄ SCH ₃
1-56	-CN	-SOCF ₃	-CH ₂ OCH ₂ C≡CH	-CH ₂ OCH ₂ C≡CH
1-57	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ SO ₂ Ph	-CH ₂ OCH ₃
1-58	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ CN	-CH ₂ OCH ₃
1-59	-CN	-SOCF ₃	-CH ₂ OCH ₂ CH=CH ₂	-CH ₂ OCH ₃
1-60	-CN	-SOCF ₃	-CH ₂ SOC ₂ H ₅	-CH ₂ SO ₂ C ₂ H ₅
1-61	-CN	-SOCF ₃	-CH ₂ OCH ₂ PO(C ₂ H ₅) ₂	-CH ₂ OCH ₂ PO(C ₂ H ₅) ₂
1-62	-CN	-SOCF ₃	-CH ₂ OCHCH ₃ CN	-CH ₂ OCHCH ₃ CN
1-63	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ CH=CH	-CH ₂ OC ₂ H ₄ CH=CH
1-64	-CN	-SOCH ₃	-CH ₂ OCH ₂ CH=CH ₂	-CH ₂ OCH ₂ CH=CH ₂
1-65	-CN	-SOCH ₃	-CH ₂ OCH ₂ CH≡CH	-CH ₂ OCH ₂ CH≡CH
1-66	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ CH=CH ₂	-CH ₂ SCH ₃
1-67	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ CH=CH ₂	-CH ₂ OC ₂ H ₄ CH=CH ₂
1-68	-CN	-SOCF ₃	-CH ₂ OCH ₂ CHOHCH ₂ SCH ₃	-CH ₂ SCH ₃
1-69	-CN	-SOCF ₃	-CH ₂ OC ₂ H ₄ OCH(CH ₃) ₂	-CH ₂ OC ₂ H ₄ OCH(CH ₃) ₂
1-70	-CN	-SOCF ₃	-CH ₂ OCH ₂ COCH ₃	-CH ₂ SCH ₃
1-71	-CN	-SOCF ₃	-CH ₂ OCH ₂ COCH ₃	-CH ₂ OCH ₂ COCH ₃
1-72	-CN	-SOCF ₃	-CH ₂ OCH ₂ CO ₂ CH ₃	-CH ₂ OCH ₂ CO ₂ CH ₃
1-73	-CN	-SOCH ₂ F	-CH ₂ OCH ₂ C≡CH	-CH ₂ OCH ₂ C≡CH
1-74	-CN	-SOCF ₃	-CH ₂ OC ₇ H ₁₅	-CH ₂ OCH ₃
1-75	-CN	-SOCHF ₂	-CH ₂ OCH ₂ C≡CH	-CH ₂ OCH ₂ C≡CH
1-76	-CN	-SOCF ₃	-CH ₂ SC ₂ H ₅	-CH ₂ SC ₂ H ₅

* Sulfoxide is the (R) enantiomer.

** Sulfoxide is the (S) enantiomer.

compounds of formula I where R^1 is $-\text{CN}$, and W is C-Cl providing the following compounds:



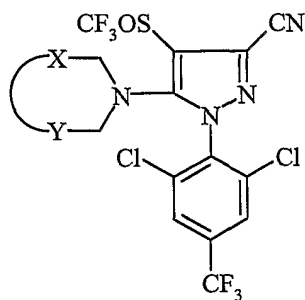
I-2

5

Cmpd. No	R^2	R^3	R^4	$-\text{A-X-R}^5$	$-\text{B-Y-R}^6$
2-1	$-\text{CF}_3$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-2	$-\text{CHF}_2$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-3	$-\text{CH}_2\text{F}$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-4	$-\text{CH}_3$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-5	$-\text{Br}$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-6	$-\text{Cl}$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-7	$-\text{NO}_2$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-8	$-\text{C}(\text{CH}_3)_3$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-9	$-\text{Ph}$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-10	$-\text{NHC}_3\text{H}_7$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-11		$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-12	$-\text{CO}_2\text{C}_2\text{H}_5$	$-\text{Cl}$	$-\text{Cl}$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-13	$-\text{CHF}_2$	$-\text{Cl}$	$-\text{OCF}_3$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-14	$-\text{CH}_2\text{F}$	$-\text{Cl}$	$-\text{OCF}_3$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-15	$-\text{CH}_3$	$-\text{Cl}$	$-\text{OCF}_3$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-16	$-\text{SOC}_2\text{H}_5$	$-\text{Cl}$	$-\text{OCF}_3$	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-17	$-\text{SOCF}_3$	$-\text{Cl}$	$-\text{OCF}_3$	$-\text{C}_2\text{H}_4\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-18	$-\text{SOCF}_3$	$-\text{Br}$	$-\text{CF}_3$	$-\text{C}_2\text{H}_4\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-19	$-\text{SOCF}_3$	$-\text{CH}_3$	$-\text{CF}_3$	$-\text{C}_2\text{H}_4\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$
2-20	$-\text{SOCH}_3$	$-\text{Cl}$	OCF_3	$-\text{CH}_2\text{OCH}_3$	$-\text{CH}_2\text{OCH}_3$

10

compounds of formula I where R^1 is $-\text{CN}$, R^2 is SOCF_3 , W is C-Cl, R^3 is Cl, R^4 is CF_3 , R^5 and R^6 are taken together to form a ring selected from (1) – (12), R^{20} is hydrogen and p is 0 providing the following compounds:



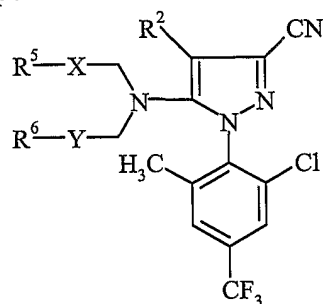
I-3

Cmpd. No	Ring Formula	n	R ²¹	R ²²
3-1	(1)	-	-	-
3-2	(7)	-	-	-
3-3	(2)	-	-	-
3-4	(6)	0	-	-
3-5	(3)	-	-	-
3-6	(4)	-		-
3-7	(5)	-		-
3-8	(8)	0	-	-
3-9	(1)	-	-	-
3-10	(9)	-	-	H
3-11	(10)	-	H	-
3-12	(11)	0	-	-
3-13	(12)	0	-	-
3-14	(12)	2	-	-
3-15	(9)	-	-	-CH ₂ OCH ₃
3-16	(11)	2	-	-
3-17	(12)	1	-	-
3-18*	(9)	-	-	-CH ₂ SCH ₃
3-19**	(9)	-	-	-CH ₂ SCH ₃
3-20	(9)	-	-	-CH ₂ SCH ₃

5 * 5-[(6R)-6-(methylthiomethyl)(1,5,3-dioxazaperhydroepin-3-yl)]-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole-3-carbonitrile

** 5-[(6S)-6-(methylthiomethyl)(1,5,3-dioxazaperhydroepin-3-yl)]-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole-3-carbonitrile

- 5 compounds of formula I where R¹ is -CN, and W is C-CH₃, R³ is Cl, and R⁴ is CF₃ providing the following compounds:



I-4

10

Cmpd. No	R ²	-A-X-R ⁵	-B-Y-R ⁶
4-1	-SOCF ₃	-CH ₂ SCH ₃	-CH ₂ SCH ₃
4-2	-SOCF ₃	-CH ₂ OC ₂ H ₅	-CH ₂ OC ₂ H ₅
4-3	-CF ₃	-CH ₂ OCH ₃	-CH ₂ OCH ₃
4-4	-SOCH ₃	-CH ₂ SCH ₃	-CH ₂ SCH ₃
4-5	-SOC ₂ H ₅	-CH ₂ SCH ₃	-CH ₂ SCH ₃

The following table sets forth physical characterizing data for certain compounds of formula I of the present invention. The test compounds of formula I

- 15 are identified by numbers that correspond to those in Table 1:

Table 2
5-Di-(substituted)aminopyrazole Derivatives
Compound Characterization

20

Characterizing Data					
Cmpd. No.	Emperical Formulae	Melting point (°C) of solids or Physical State	Cmpd. No.	Emperical Formulae	Melting point (°C) of solids or Physical State
1-1	C ₁₈ H ₁₆ Cl ₂ F ₆ N ₄ O ₃ S ₃	OIL	1-3	C ₁₆ H ₁₂ Cl ₂ F ₆ N ₄ O ₂	78-79
1-4	C ₁₈ H ₁₆ Cl ₂ F ₆ N ₄ O ₃ S ₃	OIL	1-5	C ₁₆ H ₁₅ Cl ₂ F ₆ N ₅ O ₄ S	143
1-6	C ₂₈ H ₂₀ Cl ₂ F ₆ N ₄ O ₃ S ₃	OIL	1-7	C ₂₈ H ₂₀ Cl ₂ F ₆ N ₄ O ₃ S	118-120
1-8	C ₂₀ H ₁₆ Cl ₂ F ₆ N ₄ O ₃ S	99-101	1-36	C ₁₆ H ₁₂ Cl ₂ F ₆ N ₄ O ₃ S ₃	120-123
1-45	C ₂₀ H ₂₀ Cl ₂ F ₆ N ₄ O ₅ S	OIL	1-46	C ₂₄ H ₃₂ Cl ₂ F ₆ N ₄ O ₃ SSi ₂	SOLID
1-47	C ₂₀ H ₁₄ Cl ₂ F ₆ N ₆ O ₃ S	OIL	1-54	C ₃₀ H ₂₄ Cl ₂ F ₆ N ₄ O ₃ S ₃	OIL

1-55	$C_{20}H_{20}Cl_2F_6N_4O_3S_3$	63-65	1-56	$C_{20}H_{12}Cl_2F_6N_4O_3S$	120-122
1-57	$C_{23}H_{18}Cl_2F_6N_4O_5S_2$	120-125	1-58	$C_{18}H_{13}Cl_2F_6N_5O_3S$	OIL
1-59	$C_{18}H_{14}Cl_2F_6N_4O_3S$	80-82	1-60	$C_{18}H_{16}Cl_2F_6N_4O_4S_3$	90-100
1-61	$C_{24}H_{30}Cl_2F_6N_4O_9P_2S$	OIL	1-62	$C_{20}H_{14}Cl_2F_6N_6O_3S$	OIL
1-63	$C_{22}H_{16}Cl_2F_6N_4O_3S$	OIL	1-64	$C_{20}H_{19}Cl_2F_3N_4O_3S$	71-72
1-65	$C_{20}H_{15}Cl_2F_3N_4O_3S$	124-126	1-66	$C_{20}H_{18}Cl_2F_6N_4O_2S_2$	OIL
1-67	$C_{22}H_{20}Cl_2F_6N_4O_3S$	OIL	1-68	$C_{20}H_{20}Cl_2F_6N_4O_3S_3$	OIL
1-69	$C_{24}H_{28}Cl_2F_6N_4O_5S$	OIL	1-70	$C_{19}H_{16}Cl_2F_6N_4O_3S_2$	OIL
1-71	$C_{20}H_{16}Cl_2F_6N_4O_5S$	OIL	1-72	$C_{20}H_{16}Cl_2F_6N_4O_7S$	OIL
1-73	$C_{20}H_{14}Cl_2F_4N_4O_3S$	110-111	1-74	$C_{22}H_{24}Cl_2F_6N_4O_3S$	OIL
1-75	$C_{20}H_{13}Cl_2F_5N_4O_3S$	122-124	1-76	$C_{18}H_{16}Cl_2F_6N_4OS_3$	OIL
3-9	$C_{15}H_8Cl_2F_6N_4O_3S$	OIL	3-10	$C_{16}H_{10}Cl_2F_6N_4O_3S$	200-209
3-12	$C_{16}H_{10}Cl_2F_6N_4OS_3$	151-155	3-13	$C_{16}H_{10}Cl_2F_6N_4O_2S_2$	192-197
3-14	$C_{16}H_{10}Cl_2F_6N_4O_4S_2$	200	3-15	$C_{18}H_{14}Cl_2F_6N_4O_4S$	FOAM
3-16	$C_{16}H_{10}Cl_2F_6N_4O_3S_3$	130-134	3-17	$C_{16}H_{10}Cl_2F_6N_4O_3S_2$	100-160
3-18	$C_{18}H_{14}Cl_2F_6N_4O_3S_2$	160-162	3-19	$C_{18}H_{14}Cl_2F_6N_4O_3S_2$	OIL
3-20	$C_{18}H_{14}Cl_2F_6N_4O_4S_2$	FOAM			

Candidate insecticides were evaluated for activity against the tobacco budworm (*Heliothis virescens* [Fabricius]) in a surface-treated diet test.

5 In this test one mL of molten (65-70°C) wheat germ-based artificial diet was pipetted into each well of a four by six (24 well) multi-well plate (ID# 430345-15.5 mm diameter x 17.6 mm deep; Corning Costar Corp., One Alewife Center, Cambridge, MA 02140). The diet was allowed to cool to ambient temperature before treatment with the candidate insecticide.

10 For a determination of insecticidal activity, solutions of the candidate insecticides were prepared for testing using a Packard 204DT Multiprobe[®] Robotic System (Packard Instrument Company, 800 Research Parkway, Meriden, CT 06450), in which the robot first diluted a standard 50 millimolar DMSO solution of the candidate insecticide with a 1:1 water/acetone solution (V/V) in a ratio of 1:7

15 stock solution to water/acetone. The robot subsequently pipetted 40 microliters of the so-prepared solution onto the surface of the diet in each of three wells in the 24 multi-well plate. The process was repeated with solutions of seven other candidate insecticides. Once treated, the contents of the multi-well plate were allowed to dry, leaving 0.25 millimoles of candidate insecticide on the surface of the diet, or a

20 concentration of 0.25 millimolar. Appropriate untreated controls containing only DMSO on the diet surface were also included in this test.

For evaluations of the insecticidal activity of a candidate insecticide at varying rates of application, the test was established as described above using sub-multiples of the standard 50 millimolar DMSO solution of candidate insecticide.

For example, the standard 50 millimolar solution was diluted by the robot with
 5 DMSO to give 5, 0.5, 0.05, 0.005, 0.0005 millimolar, or more dilute solutions of the candidate insecticide. In these evaluations there were six replicates of each rate of application placed on the surface of the diet in the 24 multi-well plate, for a total of four rates of application of candidate insecticide in each plate.

In each well of the test plate was placed a second instar tobacco budworm
 10 larvae, weighing approximately five milligrams. After the larvae were placed in each well, the plate was sealed with clear polyfilm adhesive tape. The tape over each well was perforated to ensure an adequate air supply. The plates were then held in a growth chamber at 25 °C and 60% relative humidity for five days (light 14 hours/day).

15 After the five-day exposure period insecticidal activity for each rate of application of candidate insecticide was assessed as percent inhibition of insect weight relative to the weight of insects from untreated controls, and percent mortality when compared to the total number of insects infested.

Insecticidal activity data at selected rates of application from this test are
 20 provided in Table 3. The test compounds of formula I are identified by numbers that correspond to those in Table 1.

Table 3
 Insecticidal Activity of Certain 5-Di-(substituted)aminopyrazole Derivatives When
 Applied to the Surface of the Diet of Tobacco Budworm
 25 (*Heliothis virescens* [Fabricius])

Cmpd. No.	Percent Mortality	Percent Growth Inhibition	Cmpd. No.	Percent Mortality	Percent Growth Inhibition
1-1	100	100	1-2	100	100
1-3	100	100	1-5	100	100
1-6	100	100	1-7	100	100
1-8	100	100	1-36	83	100
1-57	100	100	1-58	100	100
1-60	100	100	1-61	100	100
1-62	100	100	1-63	100	100
1-76	100	100	3-10	50	94
3-12	100	100	3-13	100	100

3-14	100	100	3-15	100	100
3-16	100	100	3-17	100	100

Concentration of the candidate insecticide on the surface of the diet is 0.25 millimolar

5 As set forth in Table 3, all of the tested compounds of the present invention provided insecticidal activity against the tobacco budworm, with many of the compounds providing 100% mortality and/or 100% growth inhibition.

Candidate insecticides were evaluated for insecticidal activity by observing mortality in a population of treated cotton aphid (*Aphis gossypii*) on cotton plant leaf
10 discs when compared to like populations of untreated cotton aphid on cotton plant leaf discs. These tests were conducted in the following manner:

Three week to one month-old cotton plants (*Gossypium hirsutum*) were prepared for infesting by cutting off the cotyledons and new true leaf growth, leaving the oldest two true leaves. The prepared test plant was infested with cotton
15 aphids by translocation from cotton plants grown in a cotton aphid colony. The wells of clear 128-well trays (CD-International, Pittman, New Jersey) were filled with 1 mL of a warm, aqueous 3% agar solution and allowed to cool to ambient temperature. The aphid infested cotton leaves were removed from the plants and placed bottom side up on a cutting platform. Circular discs were cut from the
20 infested leaves and placed bottom side up onto the cooled agar gel, one disc per well. Each leaf disc was visually inspected to assure that a minimum of 10 live aphids were present. A 50 mM stock solution of the test compound was prepared by dissolving the appropriate amount of the test compound in DMSO. A solution comprising 1000 part per million (ppm) of each test compound was prepared by
25 dissolving 10 µl of the stock solution in 140 µl of an aqueous 0.003% Kinetic® (a nonionic wetter/spreader/penetrant adjuvant, Helena Chemical Company, Collierville, Tennessee) solution. If needed, the solution of 1000 ppm of test compound was serially diluted with a solution consisting of 66mL of DMSO and 30 µl of Kinetic® in 934 mL of water (diluting solution) to provide solutions of each
30 test compound for lower rates of application, for example, 300 ppm, 100 ppm, 30 ppm, or 10 ppm. Each replicate infested test plant disc was sprayed with 10 µl of the test solution at about 8 psi for 1 second. For comparison purposes, a solution of a standard, such as bifenthrin, prepared in a manner analogous to that set forth

above, as well as an aqueous solution of 0.003% Kinetic® containing no test compound and the diluting solution containing no test compound were also sprayed onto infested test plant discs. Upon completion of spraying the solutions of test compound, the solution of standard, and the solutions containing no test compound, the plant discs were allowed to dry. Upon completion of drying, the test trays were covered with a plastic film. Three slits were made in the film over each well to allow air into each well. The test trays were placed in a biochamber (25°C, 16 hours light, 8 hours of dark and 35-40% relative humidity) for three days. After this time, each plant disc was assessed for percent mortality caused by the test compound when compared to the population of aphids that was infested onto the test plant discs containing no test compound. A test compound was designated as possessing insecticidal activity (SA) if there was 40% to 75% mortality of cotton aphid on plant discs sprayed with that compound. If there was 75% mortality or greater of the cotton aphid, a test compound was designated as being more insecticidally active (A). If there was 40% mortality or less of the cotton aphid, the test compound was termed as inactive (I).

An assessment of the insecticidal activity at selected rates of application from this test is provided in Table 4. The test compounds of formula I are identified by numbers that correspond to those in Table 1.

Table 4

The Following Compounds Of The Present Invention Reduced The Population Of Cotton Aphid By 40 to 100% When Applied At An Application Rate Of 1000ppm Or Less To Infested Cotton Leaf Discs

Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.
1-2	1-3	1-4	1-6	1-7	1-54	1-57	1-58	1-61	1-62
1-76	3-10	3-12	3-13	3-14	3-15	3-16	3-17		

Candidate insecticides were evaluated for insecticidal activity by observing mortality in a population of cotton aphid (*Aphis gossypii*) on treated cotton plants when compared to like populations of cotton aphid on untreated plants. These tests were conducted in the following manner:

For each rate of application of test compound, two seven-to-ten days old cotton seedlings (*Gossypium hirsutum*) grown in 7.6 cm diameter pots were selected for the test. Each test plant was infested with about 120 adult cotton aphids by placing onto each test plant cuttings of leaves from cotton plants grown in a cotton aphid colony. Once infested, the test plants were maintained for up to about 12 hours to allow complete translocation of the aphids onto the test plant. A solution comprising 1000 part per million (ppm) of each test compound was prepared by dissolving 10 milligrams of the test compound in 1 mL of acetone. Each solution was then diluted with 9 mL of a solution of 0.03 mL of polyoxyethylene(10) isooctylphenyl ether in 100 mL of water. About 2.5 mL of solution of each test compound was needed to spray each replicate of test plant (5 mL total for each test compound). If needed, the solution of 1000 ppm of test compound was serially diluted with a solution of 10% acetone and 300 ppm of polyoxyethylene(10) isooctylphenyl ether in water to provide solutions of each test compound for lower rates of application, for example, 300 ppm, 100 ppm, 30 ppm, or 10 ppm. Each replicate of test plant was sprayed with the solutions of test compound until run-off on both the upper and lower surfaces of the leaves. All the test plants were sprayed using a DeVilbus Atomizer Model 152 (Sunrise Medical, Carlsbad, CA) at a pressure of about 0.63-0.74 kilogram per square centimeter from a distance of about 30.5 centimeters from the test plants. For comparison purposes, a solution of 10% acetone and 300 ppm of polyoxyethylene(10) isooctylphenyl ether in water containing no test compound was also sprayed onto control test plants. Upon completion of spraying the solutions of test compound and the solution containing no test compound, the plants were allowed to dry. Upon completion of drying, the test and control plants were placed in a tray containing about 2.5 centimeters of water, where they were maintained in a growth chamber for 72 hours. After this time, each plant was assessed for percent mortality caused by the test compound when compared to the population of aphids that was infested onto the test plants prior to treatment with test compound. A test compound was designated as possessing insecticidal activity (SA) if there was 40% to 75% mortality of cotton aphid on plants sprayed with that compound. If there was 75% mortality or greater of the cotton aphid, a test compound was designated as being more insecticidally

active (A). If there was 40% mortality or less of the cotton aphid, the test compound was termed as inactive (I).

An assessment of the insecticidal activity at selected rates of application from this test is provided in Table 4A. The test compounds of formula I are
5 identified by numbers that correspond to those in Table 1.

Table 4A
The Following Compounds Of The Present Invention Reduced The Population Of
Cotton Aphid (*Aphis gossypii*) Between 40% and 100% When Applied At An
10 Application Rate Of 1000ppm Or Less On Infested Cotton Plants

Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.
1-1	1-2	1-5	1-36	1-46	1-55	1-57	1-60	1-62	1-63
1-64	1-65	1-66	1-67	1-68	1-69	1-70	1-71	1-72	1-73
1-74	1-76	3-10	3-17	3-19	3-20				

As set forth in Tables 4 and 4A, the tested compounds of the present
15 invention reduced the aphid population by at least 40% at an application rate of 1000ppm or less.

Candidate insecticides were evaluated for insecticidal activity by observing mortality in a population of silverleaf whitefly (*Bemisia argentifolii*) on treated cotton plant cotyledons when compared to like populations of silverleaf whitefly on
20 untreated plant cotyledons. These tests were conducted in the following manner:

For each rate of application of test compound, two four to six days old cotton seedlings (*Gossypium hirsutum*) grown in 3-inch diameter pots were selected for the test. Each test plant was sprayed with a test solution comprising 300 part per million (ppm), or less, of each test compound prepared by dissolving 12 milligrams of the
25 test compound in 4 mL of acetone. Each solution was then diluted with 36 mL of a surfactant and water solution prepared by dissolving 0.03 gm of Triton X-100[®] surfactant in 100 mL of distilled water, providing a stock test solution of 300 ppm. About 2.5 mL of solution of each test compound was needed to spray each replicate of test plant (5 mL total for each test compound). If needed, the solution of 300 ppm
30 of test compound was diluted with a solution of 10% acetone and 300 ppm of Triton X-100[®] surfactant in water to provide solutions of each test compound for lower

rates of application, for example, 100 ppm, 30 ppm, or 10 ppm. Each replicate of test plant was sprayed with the solutions of test compound until run-off on both the upper and lower surfaces of the leaves. All the test plants were sprayed using a DeVilbus Atomizer Model 152 (Sunrise Medical, Carlsbad, CA) at a pressure of about 0.63-0.74 kilogram per square centimeter from a distance of about 30.5 centimeters from the test plants. Upon completion of spraying the solutions of test compound and the solution containing no test compound, the plants were allowed to dry. Upon completion of drying, the test plants were excised at the soil surface and placed in a 1 ounce plastic cup containing a 2.5 cm filter paper moistened with 50 microliters of distilled water. Whiteflies (25-50) were added to each cup and a lid was placed on each. The test cups were maintained in a growth chamber for 72 hours at 70% relative humidity (light 12 hours/day). After this time, each test was assessed for percent mortality caused by the test compound when compared to the population of whiteflies that were infested onto the test plants. A test compound was designated as possessing insecticidal activity (SA) if there was 40% to 75% mortality of whiteflies on plants sprayed with that compound. If there was 75% mortality or greater of whiteflies, a test compound was designated as being more insecticidally active (A). If there was 40% mortality or less of the cotton aphid, the test compound was termed as inactive (I).

An assessment of the insecticidal activity at selected rates of application from this test is provided in Table 5. The test compounds of formula I are identified by numbers that correspond to those in Table 1.

Table 5
The following Compounds of The Present Invention Reduced the Population of Silverleaf Whitefly (*Bemisia argentifolii*) by 40% to 100% When Applied at an Application Rate of 300ppm or Less

Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.
1-1	1-2	1-3	1-5	1-6	1-7	1-8	1-36	1-45	1-47
1-55	1-56	1-58	1-59	1-66	1-67	1-68	1-69	1-70	1-71
1-74	1-76	3-9	3-10	1-12	3-14	3-15	3-17	3-19	3-20

Candidate insecticides were evaluated for insecticidal activity by observing mortality in a population of tarnished plant bug nymphs (*Lygus lineolaris*) on treated broccoli plant leaves when compared to like populations of tarnished plant bug on untreated plant leaves. These tests were conducted in the following manner:

- 5 For each rate of application of test compound, four ten to fifteen days old broccoli seedlings (*Brassica oleracea*) grown in 3-inch diameter pots were selected for the test. Each test plant was sprayed with a test solution comprising 300 part per million (ppm), or less, of each test compound prepared by dissolving 12 milligrams of the test compound in 4 mL of acetone. Each solution was then diluted with 36
- 10 mL of a surfactant and water solution prepared by dissolving 0.03 gm of Triton X-100[®] surfactant in 100 mL of distilled water, providing a stock test solution of 300 ppm. About 2.5 mL of solution of each test compound was needed to spray each replicate of test plant (10 mL total for each test compound). If needed, the solution of 300 ppm of test compound was diluted with a solution of 10% acetone and 300
- 15 ppm of Triton X-100[®] surfactant in water to provide solutions of each test compound for lower rates of application, for example, 100 ppm, 30 ppm, or 10 ppm. Each replicate of test plant was sprayed with the solutions of test compound until run-off on both the upper and lower surfaces of the leaves. All the test plants were sprayed using a DeVilbus Atomizer Model 152 (Sunrise Medical, Carlsbad, CA) at a
- 20 pressure of about 0.63-0.74 kilogram per square centimeter from a distance of about 30.5 centimeters from the test plants. Upon completion of spraying the solutions of test compound and the solution containing no test compound, the plants were allowed to dry. Upon completion of drying, the treated foliage was removed and two leaves were placed into an 8 ounce unwaxed paper cup which contained a one
- 25 inch piece of cut cotton wick, moistened by soaking for five seconds with distilled water. Four late second to early third instar tarnished plant bug nymphs were placed into each cup and a lid was placed on each. The test cups were maintained in a growth chamber for 72 hours at 70% relative humidity (light 12 hours/day). After this time, each test was assessed for percent mortality caused by the test compound
- 30 when compared to the population of tarnished plant bug nymphs that were infested onto the test plant leaves. A test compound was designated as possessing insecticidal activity (SA) if there was 40% to 75% mortality of cotton aphid on plants sprayed with that compound. If there was 75% mortality or greater of the

cotton aphid, a test compound was designated as being more insecticidally active (A). If there was less than 40% mortality of the cotton aphid, the test compound was termed as inactive (I).

An assessment of the insecticidal activity at selected rates of application from this test is provided in Table 6. The test compounds of formula I are identified by numbers that correspond to those in Table 1.

Table 6
The Following Compounds of The Present Invention Reduced the Population of Tarnished Leaf Bug Nymphs (*Lygus lineolaris*) By 40% to 100 % When Applied at an Application Rate of 300ppm or Less

Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.	Cmpd. No.
1-1	1-2	1-3	1-4	1-6	1-8	1-36	1-45	1-46	1-55
1-56	1-57	1-58	1-59	1-60	1-61	1-62	1-63	1-66	1-70
1-72	1-73	1-76	3-9	3-12	3-13	3-14	3-15	3-17	3-18
3-19	3-20								

Candidate insecticides were evaluated for insecticidal activity by observing mortality in a population of Formosan termite (*Coptotermes formosanus*) on treated sandy clay loam top soil when compared to like populations of Formosan termite on untreated sandy clay loam top soil. These tests were conducted in the following manner:

For a test rate of application of 300 parts per million (ppm), a test solution was prepared by dissolving 9 mg of the test compound in 3 mL of acetone. Application of this solution to 30 grams of sandy clay loam top soil provided a concentration of 300 ppm of the test compound in the soil ($300 \text{ ppm} = 0.3 \text{ mg/g} \times 30 \text{ gm of top soil} = 9.0 \text{ mg of test compound}$). If needed, the initial test solution was serially diluted with acetone to provide solutions of each test compound for lower rates of application onto 30 grams of sandy clay loam top soil, for example, 100 ppm, 30 ppm, 10 ppm, 3 ppm, 1 ppm, 0.3 ppm or 0.1 ppm.

For each test rate, 3 mL of the test solution was added to 30 grams of unsterilized sandy clay loam top soil in a container and mixed well. The treated soil was allowed to dry at ambient temperature in a hood for 30 minutes. Three mL of

distilled water was added to the treated soil providing a soil moisture of 10%. The treated soil was distributed equally into three 60 x 15 mm Petri dishes. The soil in each Petri dish was infested with 10 adult Formosan termites after residual periods of 0 days.

5 For comparison purposes, soil samples containing 10% moisture as described above were prepared from an untreated sandy clay loam top soil sample (untreated check). Upon completion of infestation the tops were placed on the Petri dishes and the Petri dishes were placed in a growth chamber where they were maintained in the dark for 7 days at 80% relative humidity.

10 During this time, each test was assessed daily up to 7 days after infestation (DAI) for percent mortality caused by the test compound when compared to the population of termites that were infested onto the control soil tests containing no test compound. Termites are classified as dead if they fail to show movement when probed.

15 An assessment of the insecticidal activity at selected rates of application from this test is provided in Table 7 below. The test compounds of formula I are identified by numbers that correspond to those in Table 1.

Table 7

20 Termiticidal Activity of The Following Compounds of The Present Invention when Applied at an Application Rate of 30ppm Infesting at Day Zero After Treatment

Cmpd. No.	7 DAI % Mortality
1-6	97
1-7	100
1-8	100
1-36	83
1-56	100
3-10	100
3-12	100
3-14	100
3-15	100
Untreated Check	0

25

Candidate insecticides were evaluated for mammalian toxicity in a GABA receptor test. Rat brains were homogenized with physiological saline (same pH as in the rat plasma). A portion of this suspension (0.1 mL) was mixed with a

radioligand [4'-ethynyl-4-n-propyl bicycloorthobenzoate (EBOB)]. Tubes containing this mixture and a test compound were compared with a reference (tubes with this mixture but without test compound).

5 All tubes were incubated (90 minutes, 20°C). The content was filtered and the radioactivity remaining on the filter was determined. The concentration of the test compound that inhibited 50% of the controlled binding was the IC-50 of the compound.

10 The radioligand binds to a site within the known GABA receptor channel. If there is no test compound, the radioligand does bind; if there is a toxic compound effective on the same site, the amount of radioligand is reduced because the test compound replaces the radioligand.

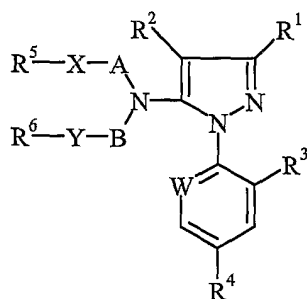
15 In the above in vivo test on the GABA receptor channel, representative compounds of the invention were inactive or weakly active at a very high concentration (high IC-50), which shows that the compounds are still safe for mammals even when toxic to pests.

While this invention has been described with an emphasis upon preferred embodiments, it will be understood by those of ordinary skill in the art that variations of the preferred embodiments may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein.

20 Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the following claims.

What is claimed is:

Claim 1. A compound of formula I



I

wherein

W is C-halogen, C-CH₃, C-CH₂F, C-CHF₂, C-CF₃, C-NO₂ or N;

R¹ is selected from halogen, cyano, (C₁-C₄)alkyl, (C₁-C₄)haloalkyl, -S(O)_nR¹⁰, formyl, acetyl, nitro, -C(S)NH₂, -C(=NNH₂)NH₂; or R¹ is -CR⁷=N-O-Y¹, wherein R⁷ is hydrogen, alkyl or R⁷ and Y¹ may be taken together to form a 5 or 6 member ring or R⁷ is -NR⁸R⁹, wherein R⁸ and R⁹ are independently hydrogen or alkyl and Y¹ is hydrogen, alkenyl, alkynyl, formyl, alkylcarbonyl, cycloalkylcarbonyl, haloalkylcarbonyl, aroyl, arylalkylcarbonyl, alkylsulfonyl, arylsulfonyl, haloalkylcarbonyl, aminoalkylcarbonyl, alkylaminoalkylcarbonyl, dialkylaminocarbonyl, alkoxyalkylcarbonyl, arylalkoxycarbonyl, alkylthioalkylcarbonyl, alkylsulfonylalkylcarbonyl, arylthioalkoxycarbonyl, N-alkylcarbamoyl, N-arylcarbamoyl, N-alkylthiocarbamoyl, N-arylthiocarbamoyl, alpha-hydroxyarylalkylcarbonyl, hydroxyalkylcarbonyl, carboxyalkylcarbonyl, alkoxyalkylcarbonyl, -P(=O)(O-alkyl)₂, -P(=S)(O-alkyl)₂, -P(=O)(S-alkyl)₂, trialkylsilyl, alkylcarbonylaminoalkylcarbonyl, alkylcarbonyloxyalkylcarbonyl, aryl, pyridinyl, pyrimidinyl, -C(=O)S-alkyl, -C(=O)S-aryl, -C(=O)S-alkylaryl, alkoxyalkoxycarbonyl, alkylthioalkoxycarbonyl, alkylsulfonylalkoxycarbonyl, arylthioalkoxycarbonyl, alkoxyalkyl, aryloxyalkyl and aryloxyalkylalkylcarbonyl; or alkyl or haloalkyl, optionally substituted by alkoxy, alkoxyalkyl, carboxy, cyano, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylthio, nitro, alkylsulfinyl, alkylsulfonyl, alkylcarbonyl, amino, alkylamino, dialkylamino, hydroxy, alkylcarbonylamino or alkylcarbonyloxy;

R^2 is selected from hydrogen, halogen, $-S(O)_nR^{10}$, $(C_1-C_4)alkyl$, $(C_1-C_4)haloalkyl$, $(C_3-C_5)alkenyl$, $(C_3-C_5)haloalkenyl$, $(C_3-C_6)cycloalkyl$, $(C_3-C_6)halocycloalkyl$, $(C_3-C_5)alkynyl$, aryl, heteroaryl, $-NR^8R^9$, $-CO_2R^{15}$, $-CR^7=N-O-Y^1$, nitro or cyano;

n is an integer selected from 0, 1 and 2;

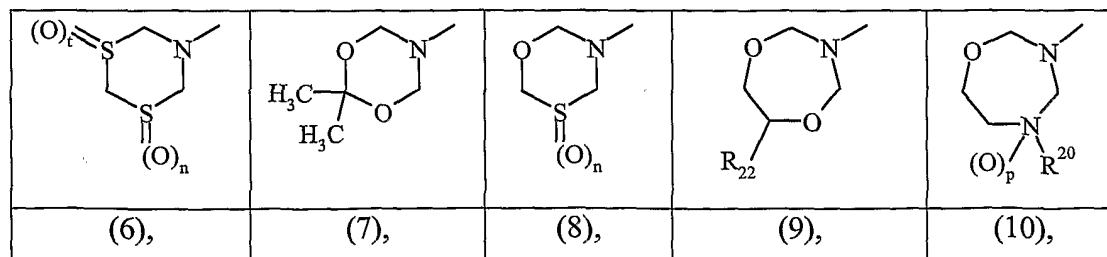
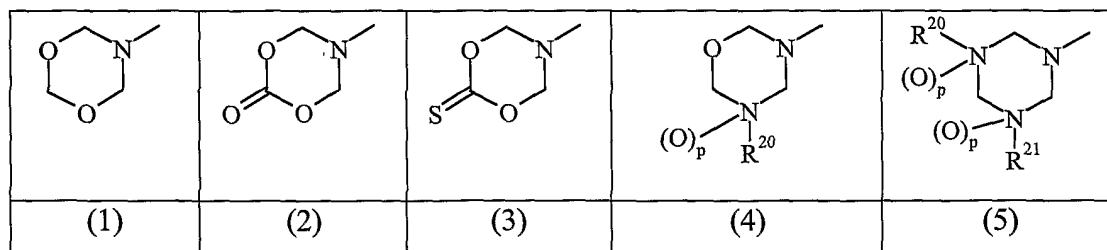
R^3 is hydrogen, halogen, cyano, formyl, acetyl, alkyl, haloalkyl or nitro;

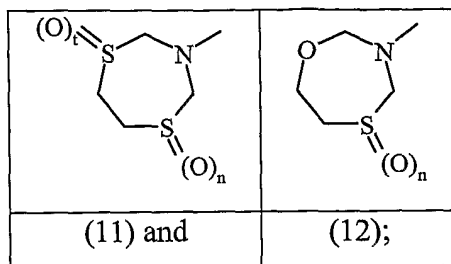
R^4 is halogen, $(C_1-C_4)alkyl$, $(C_1-C_4)haloalkyl$, $(C_3-C_5)alkenyl$, $(C_3-C_5)alkynyl$, $(C_1-C_4)alkoxy$, $(C_1-C_4)haloalkoxy$, $-S(O)_nhaloalkyl$ or $-SF_5$;

A and B are independently selected from alkylene and haloalkylene;

X and Y are independently selected from O , $N-R^{11}$, $N(O)-R^{13}$, $SiR^{10}R^{10}$, and $S(O)_n$;

R^5 and R^6 are independently selected from hydrogen, $(C_3-C_5)alkenyl$, $(C_3-C_5)haloalkenyl$, $(C_3-C_5)alkynyl$, $(C_3-C_5)haloalkynyl$, $(C_3-C_6)cycloalkyl$, $-(CH_2)_qR^{12}$, $-(CH_2)_qR^{13}$ and $-NR^{15}R^{16}$; or is $(C_1-C_7)alkyl$ unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkoxy, haloalkoxy, alkenyloxy, haloalkenyloxy, alkynyloxy, haloalkynyloxy, trialkylsilyl, cycloalkyl, $-S(O)_nR^{13}$, $-CN$, $-NO_2$, $-OH$, $-OR^{12}$, $-OR^{14}$, $-COR^{15}$, $-NR^{15}COR^{16}$, $-P(=O)(O-alkyl)_2$, $-P(=S)(O-alkyl)_2$, $-NR^{15}SO_2R^{13}$, $-CONR^{15}R^{16}$, $-NR^{15}R^{16}$, $-S(O)_nR^{12}$, $-S(O)_nR^{14}$, and $-CO_2R^{15}$; or R^5 and R^6 may be taken together to form a ring selected from the following:





p is an integer selected from 0 or 1;

q is an integer selected from 0, 1, 2 and 3;

t is an integer selected from 0, 1 and 2;

R¹⁰ is alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl or halocycloalkyl;

R¹¹ hydrogen, alkyl and haloalkyl;

R¹² is phenyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, -CN, -NO₂, -S(O)_nR¹³, -COR¹⁶, -COR¹⁸, -CONR¹⁵R¹⁶, -SO₂NR¹⁵R¹⁶, -NR¹⁵R¹⁶, -OH, -SO₃H and alkylideneimino;

R¹³ is haloalkyl, alkylcarbonyl or alkoxy carbonyl;

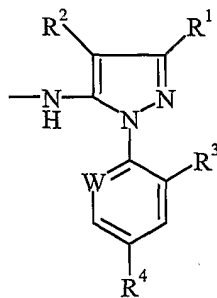
R¹⁴ is heterocyclyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, -CN, -NO₂, -S(O)_nR¹³, -OH and -CO₂alkyl;

R¹⁵ and R¹⁷ are each independently hydrogen, alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl, cycloalkylalkyl, -(CH₂)_qR¹⁸ or -(CH₂)_qR¹⁴;

R¹⁶ and R¹⁹ are each independently hydrogen, alkyl, haloalkyl, cycloalkyl or cycloalkylalkyl;

R¹⁸ is phenyl unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, -CN, -NO₂, -S(O)_nR¹³ and -NR¹⁶R¹⁹;

R²⁰ and R²¹ are independently selected from hydrogen, alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl, cycloalkylalkyl, -(CH₂)_qR¹⁸, -(CH₂)_qR¹⁴, -COalkyl, -S(O)_nalkyl or



(13);

R²² is hydrogen, alkyl, alkoxy, alkoxyalkyl, alkylthioalkyl or alkylsulfinylalkyl; and each heterocyclyl in the above-mentioned radicals is independently a heterocyclic radical having 3 to 7 ring atoms and 1, 2 or 3 hetero atoms in the ring selected from the group consisting of N, O and S;

and

pesticidally acceptable salts thereof;

provided that when R¹ is cyano and R² is -S(O)_nR¹⁰, then A and B are other than methylene, X and Y are other than O and R⁵ and R⁶ are other than methyl.

Claim 2 A compound of claim 1, wherein

W is C-halogen;

R¹ is cyano;

R² is, -S(O)_nR¹⁰ or haloalkyl;

R³ is halogen;

R⁴ is haloalkyl; and

A and B are each -CH₂-;

X and Y are each O or S(O)_n; and

R⁵ and R⁶ are each alkyl or are taken together to form a ring of formula (9), formula (11) or formula (12).

Claim 3. A compound of claim 2, wherein

W is C-Cl;

R² is, -S(O)CF₃ or CF₃;

R³ is chlorine;

R⁴ is CF₃;

X and Y are each O or S(O)_n where n is 0; and

R⁵ and R⁶ are each methyl or ethyl.

Claim 4. A composition comprising an insecticidally effective amount of a compound of claim 1 and at least one agriculturally acceptable extender or adjuvant.

Claim 5. The insecticidal composition of claim 4, further comprising one or more additional compounds selected from the group consisting of pesticides, plant growth regulators, fertilizers and soil conditioners.

Claim 6. A method of controlling insects, comprising applying an insecticidally effective amount of a composition of claim 4 to a locus where insects are present or are expected to be present.

Claim 7. A method of controlling insects, comprising applying an insecticidally effective amount of a composition of claim 5 to a locus where insects are present or are expected to be present.

Claim 8. A composition comprising a general household pesticidally effective amount of a compound of claim 1 and at least one acceptable extender or adjuvant.

Claim 9. The pesticidal composition of claim 8, further comprising one or more additional compounds selected from the group consisting of insecticides.

Claim 10. A method of controlling general household pests, comprising applying a pesticidally effective amount of a composition of claim 8 to a locus where general household pests are present or are expected to be present.

Claim 11. A method of controlling general household pests, comprising applying a pesticidally effective amount of a composition of claim 9 to a locus where general household pests are present or are expected to be present.

Claim 12. A composition comprising a parasitically effective amount of a compound of claim 1 and at least one acceptable extender or adjuvant.

Claim 13. The parasitic composition of claim 12, further comprising one or more additional compounds selected from the group consisting of insecticides.

Claim 14. A method of controlling animal parasites, comprising applying a parasitically effective amount of a composition of claim 12 to a locus where animal parasites are present or are expected to be present.

Claim 15. A method of controlling animal parasites, comprising applying a parasitically effective amount of a composition of claim 13 to a locus where animal parasites are present or are expected to be present.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 60452-PCT1	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/US06/22356	International filing date (<i>day/month/year</i>) 07 June 2006 (07.06.2006)	(Earliest) Priority Date (<i>day/month/year</i>) 13 June 2005 (13.06.2005)
Applicant FMC CORPORATION		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the Report

a. With regard to the **language**, the international search was carried out on the basis of:

☒
☐

the international application in the language in which it was filed.

a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☒ **Certain claims were found unsearchable** (See Box No. II)

3. ☐ **Unity of invention is lacking** (See Box No. III)

4. With regard to the **title**,

☒
☐

the text is approved as submitted by the applicant.

the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒
☐

the text is approved as submitted by the applicant.

the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No. _____

☐
☐
☐

as suggested by the applicant.

as selected by this Authority, because the applicant failed to suggest a figure.

as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US06/22356

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 2-15
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Please See Continuation Sheet
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
 2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of any additional fees.
 3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
 4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
- Remark on Protest**
- | | |
|--------------------------|---|
| ☐ | The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee. |
| ☐ | The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation. |
| ☐ | No protest accompanied the payment of additional search fees. |

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US06/22356

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C07D 231/46**(2006.01)

USPC: 548/369.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 548/369.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,812,347 B2 (ROUSSEAU et al) 2 November 2004 (02.11.2004), see entire document.	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

06 September 2006 (06.09.2006)

Date of mailing of the international search report

26 SEP 2006

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US06/22356

Continuation of Box II Reason 2:

In these claims, the numerous variables and their voluminous, complex meanings and their seemingly endless permutations and combinations plus the proviso clause make it virtually impossible to determine the full scope and complete meaning of the claimed subject matter. As presented, the claimed subject matter cannot be regarded as being a clear and concise description for which protection is sought and as such the listed claims do not comply with the requirements of PCT Article 6. Thus it is impossible to carry out a meaningful search on same. A search will be made on the first discernable invention, i.e., compound no. 1-1 in Table 1.